

Technologies of syntheses of fluorofunctional silicon compounds

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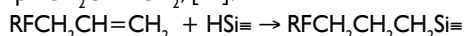
Introduction

Fluorine containing compounds have attracted much attention not only because of their influence on hydrophobic and oleophobic properties, but also because of the possibility of their use as precursors of new materials used in bio- and nanotechnology [1 ÷ 3]. Such precursors can also be the fluorine containing organosilicon derivatives. Fluorofunctional silanes are used as surfactants, modifiers of surfaces of lens and optical fibres, components of many cosmetic products or modifiers of fluorine and silicon caoutchouc. A particularly interesting range of applications is the production of oilproof, dirtproof and waterproof surfaces [4 ÷ 9] for protecting coatings like e.g. "invisible windscreen wiper", "self-cleaning windowpanes", anti-graffiti preparations, anti-foam agents and polymer materials for specific use (e.g. elements of high thermal and chemical resistance and strong anti-adhesive properties). Most of the literature on the subject has been devoted to direct surface modification by fluoroalkyltrialkoxysilanes to obtain easily cleaned surfaces [10 ÷ 12] or to endow hydrophobicity to membranes obtained from metal oxides and used in membrane distillation and for production of anti-reflective, transparent and strongly hydrophobic coatings [13].

Although the interest in strongly hydrophobic materials is high, their production with the use of fluorofunctional organosilicon compounds is still rare. The problems are high cost and difficult synthesis of compounds from this group, though their properties are ideal for production of superhydrophobic materials. The production and use of superhydrophobic materials is of top interest for many research centres and large production concerns. In particular, much effort is devoted to design and development of effective technologies for the production of superhydrophobic materials on the basis of fluorofunctional organosilicon compounds.

Methods for the synthesis of fluorofunctional silicon compounds

The main method for the synthesis of this group of compounds is based on hydrosilylation of appropriate fluorinated olefins. Because of the positive character of silicon, the olefin should contain at least a non-fluorinated vinyl group $-\text{CH}=\text{CH}_2$, and optimally a non-fluorinated allyl group $-\text{CH}_2\text{CH}=\text{CH}_2$, [14]:



In industrial scale fluorinated olefins are obtained from fluoroalkyl iodide as a precursor, which means that the olefin may contain some amount of iodine ions whose presence is unfavourable for hydrosilylation as they can poison the catalysts. The most popular catalysts of fluoro-olefin hydrosilylation are platinum compounds, in particular those with platinum(+IV) such as hexachloroplatinic acid H_2PtCl_6 , platinum(+II), e.g. $\text{PtCl}_2(\text{cod})$ or platinum(0) such as Karstedt catalyst [15, 16]. Platinum compounds show high catalytic activity in hydrosilylation of a wide group of different functional olefins, but they are susceptible to poisoning caused by the presence of contaminants [17]. The process of hydrosilylation is exothermic

and high temperature favours isomerisation of fluorinated olefins and hence a decrease in the efficiency and selectivity of the process. To protect the catalysts against a rapid increase in temperature, different solvents are used, but this procedure implies an additional stage of the process to remove the solvent. The synthesis of fluorofunctional polysiloxanes and silsesquioxanes has been already described by us in [25 ÷ 27]. When fluorocarbofunctional silanes were used, only fluorocarbofunctional chloroalkylsilanes were obtained in direct hydrosilylation, but alkoxy derivatives were obtained as a result of an additional process of alcoholysis of fluorocarbofunctional chloroalkylsilanes [18]. This implies the need to perform the process at two stages of addition and alcoholysis. Moreover, the product obtained after alcoholysis is acidified because of hydrochloric acid evolved in the process, so it should be deacidified as the acidified product is unstable (undergoes condensation). The process of synthesis of fluorocarbofunctional silanes is often conducted in a closed system [19]. From the technological point of view such reactions are very difficult not only because of the necessity of working under high pressure but also because of very low boiling points of the reagents, their high vapour pressures and aggressive properties (threat of corrosion) which means that the pressure apparatuses must be made of special and expensive materials. Analogous reactions carried out under atmospheric pressure needed much longer time.

The substrates were fluorinated alkenes and fluoroalkyl-allyl ethers and perfluoro-allyl polyethers [20]. The process was conducted in a tube reactor under elevated pressure and the main product was accompanied by many products of redistribution of the initial silane and olefins.

The methods for the synthesis of fluoroalkylalkoxysilanes described in literature require drastic conditions (high pressure and high temperature) and from the technological point of view they are very difficult, need special equipment (high-pressure reactor) and additional precautions related to the work under high pressure. Moreover, alkoxy derivatives have always been produced in a two-step process, and never in a direct hydrosilylation of fluoroalkyl-allyl ethers by trialkoxysilanes. It is known that a multistage process is expensive as it needs more energy, needs more time for completion and give a large number of waste products.

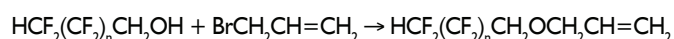
The methods for the synthesis of silane fluoro-derivatives [21, 22], siloxanes [23 ÷ 25] and silsesquioxanes [26, 27] developed by our group are based on hydrosilylation of fluoroalkyl-allyl ethers by trialkoxysilanes, hydrido(poly)siloxanes and hydridosilsesquioxanes, in mild conditions, catalysed by highly effective siloxy rhodium complex. In all procedures proposed fluorinated alcohols are used, which are much cheaper than fluoroalkyl iodides, free from contaminants and produced in Poland. The methods proposed were optimised in order to establish technologies of syntheses of a wide gamut of fluorofunctional organosilicon compounds. Irrespective of the type of the silicon precursor (containing Si-H bond), the method for the synthesis is the same, which permits preparation of

a universal technology for production of all derivatives. Of relatively greatest use are fluorofunctional silanes, which can be semi-products in the synthesis of fluorofunctional polysiloxanes (obtained as a result of condensation of fluorofunctional dilalkoxysilanes with dimethyldichlorosilanes [28]) or fluorofunctional silsesquioxanes (obtained as a result of hydrolytic condensation of fluorofunctional trialkoxysilanes [29]).

Technological process

Substrates

The substrates are: the commercially available silanes (trichloro- and triethoxysilane – P.I.W. Unisil; dichloromethyl- and dimethylchlorosilane – Gelest) and hydrogen polysiloxanes (Wacker), and oktakis(dimethylsiloxy)oktasilsesquioxane synthesised in the Poznań Science and Technology Park according to the literature procedure [30]. Fluorinated olefins are fluoroalkyl-allyl ethers, obtained from the commercially available fluorinated alcohols and allyl chloride. Synthesis of this type derivative is based on the Williamson reaction [31]:



Optimisation of the process permitted a modification of the process by using a cheaper allyl chloride instead of allyl bromide and dimethylaminopyridine instead of tetrabutyl ammonium bromide as a catalyst of phase transfer [25]. The use of the above reagents permitted a shortening of the synthesis duration by 2/3 and achieve the yield of fluoroalkyl allyl ethers at a level of 80% (the yields hitherto achieved had been 62-66%). Depending on the type of alcohol used, the method permits getting different fluorinated olefins free from iodide contaminants in good yields.

The catalyst of hydrosilylation processes was the siloxyl rhodium complex $[\{\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ designed by Professor Marciniec group [31], whose catalytic activity in hydrosilylation of olefins is much greater (even at room temperature) [32] than those of commonly used platinum complexes (Speier's, Karstedt's catalysts). Taking into account the need to separate the catalyst from the post-reaction mixture and the possibility of repeated use of the same portion of the catalyst it is recommended to use heterogeneous catalysts. A series of catalytic systems based on the siloxyl rhodium complex immobilised in different ionic liquids (in particular phosphonium and pyrylium derivatives) were designed and tested at our laboratory to be efficient catalysts of hydrosilylation also hydrosilylation of fluorinated olefins [25÷27]. The latter process is realised in the two-phase liquid-liquid system and after its completion the phases are separated by e.g. decantation.

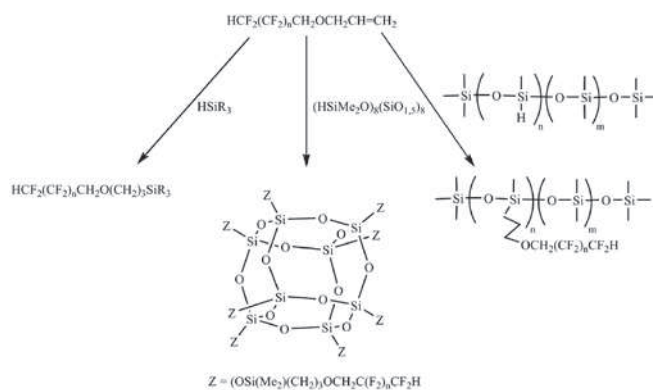
Equipment needed

The process of hydrosilylation of fluorinated olefins is carried out at a mild temperature so typical equipment can be used with no need for special apparatuses. A typical reaction system is made of a reactor (glass or metal, covered with enamel on the inside) with an external heating coat, equipped with a mechanical stirrer, reflux and dosing unit. The reactor should have a bottom outlet to facilitate phase separation. For removal of the product from above the catalytic system it is also possible to use a vacuum system connected to a receiver or an appropriate pump.

Fundamental technological solutions of hydrosilylation of fluorinated olefins

The scale of production of particular derivatives depends on the type of organosilicon substrate used (fluorofunctional silsesquioxanes are obtained in much smaller amounts than silanes or polysiloxanes),

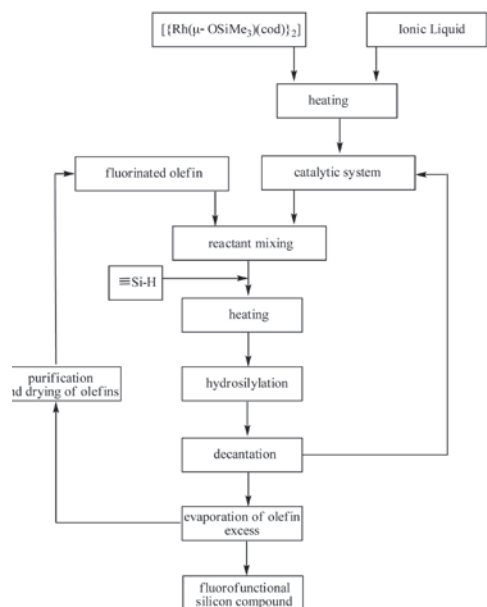
although the procedure is the same and does not need modifications. The process is universal and permits obtaining all types of fluorofunctional organosilicon derivatives, as shown in Scheme 1.



Scheme 1. The universal process of synthesis of different fluorofunctional silicon derivatives based on the hydrosilylation reaction

Within the procedures aimed at optimisation of hydrosilylation of fluoroalkyl-allyl ethers, the testing syntheses of silanes and polysiloxanes were performed in a few kilogram scales and the course of the reaction was the same as in the laboratory scale. The target product was always obtained with a high yield (90-95%). The optimisation showed that a 10% excess of the olefin should be used and the temperature of the process should be in the range 60-100°C. In view of high sensitivity of organosilicon compounds to even trace amounts of moisture (they contain Si-H bond or alkoxy groups) the olefins used must be properly dried. The catalytic system made of the siloxy rhodium complex dissolved in an ionic liquid should be prepared earlier. The optimum amount of the ionic liquid is 1% of the volume of all substrates. Too much of the ionic liquid gives a too highly diluted catalyst and too small amount of this liquid causes problems in separation of the post-reaction mixture. Sometimes to achieve full homogenisation of the system it must be heated to 60°C. In general, the procedure is as follows. A proper fluoroalkyl-allyl ether and the catalytic system are introduced into the reactor; the concentration of siloxy rhodium complex $[\{\text{Rh}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ should be 10^{-5} - 10^{-6} mol Rh per 1 mol of Si-H groups. The content is stirred and then the organosilicon substrate is introduced in doses. After this the content of the reactor is stirred and heated to 60-100°C (usually a higher temperature is used for polysiloxane systems), till the process completion, which usually takes from 1 to 4 hours. In order to separate the catalytic system, after cooling and phase separation the post-reaction mixture should be removed from above the catalyst, while the catalyst should be left in the reactor. To thus separated catalytic system a new portion substrates is introduced and the process begins anew. The catalytic system was shown not to lose its activity even after 10 times repeated use. The idea of synthesis of fluorofunctional organosilicon derivatives is presented in Scheme 2.

If a high purity of the product is needed the post-reaction mixture must be subjected to fractional distillation (it mainly refers to fluorofunctional silanes) but usually it is sufficient just to evaporate the excess olefin that should be collected and periodically purified and reused. Taking into account high efficiency of the catalytic system (short duration of the main process of hydrosilylation) and no need to perform time-consuming operations, the size of production of fluorofunctional silanes and polysiloxanes is assumed as about 10 tons per year (40 kg per charge, and one charge can be produced within a single 8-hour shift). The assumed scale of production of fluorofunctional silsesquioxanes is much smaller and is approximated as a few ten to a few hundred kilograms per year.



Scheme 2. The idea of synthesis of fluorofunctional silicon compounds

Concluding remarks

Fluorofunctional silicon compounds are very important in the syntheses of new materials and in modification of many kinds of surfaces to obtain highly oleophobic and hydrophobic coatings. The proposed fundamental technological solutions of the universal method for the synthesis of fluorofunctional silicon compounds based on the hydrosilylation processes (with the use of highly active catalytic system) of fluorinated olefins (obtained from the available fluorinated alcohols) are expected to extend the use of this group of compounds in production of new materials.

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Correction

The editors wish to apologize for the publishing of an unauthorized version of the paper by Piotr Bałczewski, Agnieszka Bodziach and Joanna Skalik titled „A new tool for synthesis of organic optoelectronic materials” (CHEMIK 2012, **66**, 1, 11-20) received on October 3, 2011 and modified by the Authors on December 2, 2011 before the peer review process, in particular, for the final form, content and graphic material contained in a published article.

The Editors