Ammonolysis of (3-chloropropyl)trimethoxysilane

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Abstract

Technological parameters of the ammonolysis of (3-chloropropyl)trimethoxysilane to (3-aminopropyl)trimethoxysilane have been determined. Influence of temperature, reaction time and the molar ratio of ammonia to (3-chloropropyl)trimethoxysilane has been examined. Influence of the parameters has been described using the following factors describing the process: the degree of conversion of (3-chloropropyl)trimethoxysilane and the selectivity of transformation to (3-aminopropyl)trimethoxysilane in relation to consumed (3-chloropropyl)trimethoxysilane.
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1. Introduction

One of the most dynamically developing branches of the chemical industry is the production of silanes containing the organic functional groups. These compounds are useful as the coupling and cross-linking agents and the auxiliaries for plastics. The chemical structure of organofunctional silanes can be represented by the general formula [1]: $(CH_3) X_{3-n} Si (CH_2)_m Y$; $n = 0$, 1, 2, $m = 0$, 2, 3 in which the functional groups are as follows:

$X = -RO, -RC(O)O, -Cl$ and

$R = -CH_3, -C_2H_5, -CH_3OCH_2CH_2$

$Y = -NH_2, -NHR, -NH(CH_2)NH_2, -NHCONH_2, -NCO, -Cl.$

Structure of organofunctional silanes results in their high reactivity both with organic and inorganic compounds. It gives ability to use these compounds as the improver agents in the plastic industry.

The application of silanes as the coupling agents in high-tech composites with "shape memory alloys" (SMA) was reported by Smith et al. [2]. It was found that a quality of the interface between SMA and the polymer matrix is the most important factor allowing to achieve the best properties of the final composite.

The alkoxysilyl derivatives are used as the key compounds in modern hybrid materials for advanced electronics and photonics [3]. Organo-inorganic thin film layers were obtained in the hydrolysis and condensation reactions between titanium alkoxides and poly(methylphenylsilane)-*co*-3-methacryloxypropyltriethoxysilane (block copolymer).

A method of preparation of the hybrids of organic and inorganic materials in a sol–gel type of the reaction described above, has found numerous new advanced applications in the recent years. Organosilica compounds used in these compositions allow to dope the matrix with biological species such as enzymes, antibodies and other proteins. The preparation of biosensors by the immobilization of acetylcholinesteraze on a silica matrix in the sol–gel reaction was described [4]. Polymethylsiloxane was used as a binding agent for the electrode matrix. The biosensors prepared in this method are used in the detectors for organophosphorous pesticides.

The synthesis of organosilicon polymers with excellent heat-resistant properties was described [5]. The thermal properties of poly[(silylene)phenylene] derivatives were examined. The incorporation of unsaturated functional groups into silicon results in an increase of the thermal resistance of polymer. The thermogravimetric analyses of obtained polymers confirmed their high thermal resistance.

A growing demand for these types of compounds is a reason of high interest in the development of new methods for their production and the improvements of the existing technologies.

The investigations of Gulinski et al. [6] and Burkus et al. [7] have resulted in patenting of the technologies and indus-

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trial production of the novel types organofunctional silanes. An important group of the discussed compounds includes the aminoderivatives including aminopropylethoxysilanes. In 1969 Golitz et al. [8] patented the methods of the manufacture of bis- and tris-(trialkoxysilyloalkylamines). The methods of the manufacture of aminoalkylsilanes are also presented in works of Kleinstuck [9], Kappler et al. [10,11], Balduf et al. [12] and Schwarz et al. [13].

The purpose of these studies was the determination of the influence of technological parameters on the ammonolysis of (3-chloropropyl)trimethoxysilane (CPTMS). The optimal technological parameters of preparation of (3-aminopropyl)trimethoxysilane (APTMS) via the ammonolysis CPTMS have been also elaborated.

The ammonolysis process of CPTMS was carried out batchwise using anhydrous liquid ammonia. This procedure requires a pressure apparatus and allows the preparation of many other useful amines [14,15]. Moreover this method enables the preparation of amines from the compounds, which require absolutely anhydrous reaction medium. Such environment is necessary in the case of alkoxysilanes because methoxy group readily undergo the hydrolysis to silanols. This reaction is a foundation of their application as the adhesion promoters or the modifiers of the inorganic surfaces [16,17].

2. Experimental

2.1. Materials

CPTMS was provided by Chemical Work in Tarnów (Poland) and used without further purification. Anhydrous ammonia pressurized in the steel cylinder was provided from Chemical Work Police (Poland).

2.2. Procedure of ammonolysis

The studies were performed in laboratory high-pressure autoclave Berghof Labortechnik GmbH with capacity of $150\,cm^3$. A few syntheses were carried out in the best technological parameters in the autoclave capacity of $1000\,cm^3$ (Lampart RT). The autoclaves were equipped with electronic temperature controllers and agitators. The autoclaves and the fittings were purged with the dry argon before the loading of substrates. The autoclave containing CPTMS was cooled to $-50\,°C$ and then filled with liquid ammonia after the removal of argon from the reaction space using apparatus shown in Fig. 1.

The charged autoclave was subsequently placed in a heating jacket and heated to the reaction temperature. After the synthesis was completed, the autoclave was again cooled to $-50\,°C$. The autoclave was taken out from the cooling bath and the outlet valve was opened in order to slowly distil off the unconverted ammonia. When the temperature reached $-10\,°C$, the purge of dry argon was started to protect the post-reaction mixture from humidity. After the heating the autoclave to $20\,°C$, three weight parts of dry toluene per one weight part of the beginning amount of CPTMS was added. The ammonium chloride was removed by the filtration and filtrate was distilled under reduced pressure.
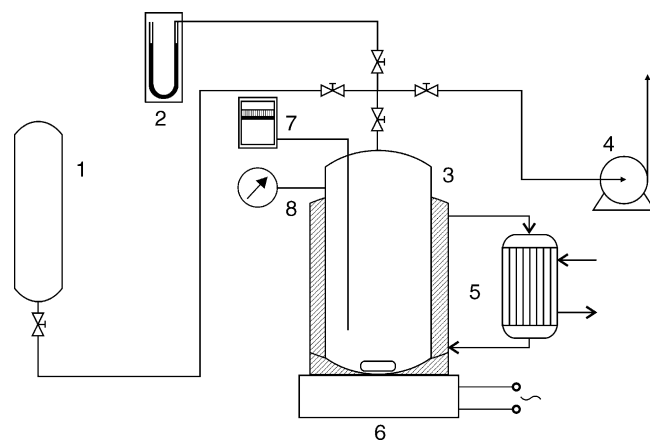

Fig. 1. Scheme of apparatus (1—ammonia cylinder, 2—mercury gauge, 3—autoclave, 4—vacuum pump, 5—kryostat/heater, 6—magnetic stirrer, 7—temperature controller, 8—manometer).

CPTMS was distilled under the pressure of 40 Torr at temperature of $97\,°C$, whereas APTMS under the pressure of 8 Torr at temperature of $62\,°C$.

2.3. Analytical methods

The concentrations of APTMS and CPTMS were determined on a GC8000[TOP] Thermoquest gas chromatograph, equipped with flame-ionization detector (FID). The analyses were carried out under the following conditions: Quadrex 007WAX column (polyethylene glycol 20 M) ($30\,m \times 0.32\,mm \times 0.5\,\mu m$); in the temperature gradient: isothermally at $60\,°C$ for 5 min then increase to $200\,°C$ at the rate of $15\,°C/min$ and isothermally for 1 min. The operating conditions for the FID were as follows: detector temperature $240\,°C$, carrier gas—helium $6\,cm^3/min$, hydrogen flow rate $20\,cm^3/min$, the flow rate of air equal to $200\,cm^3/min$. The sample injector was the type of *split-splitless* with 1:20 split rate. The temperature of the sample injector was $250\,°C$. The identification of the products of ammonolysis were performed using GC–MS methods. The quadrupol detector with electron ionisation worked in the condition: the source temperature $200\,°C$, the detector voltage 50 V, the emission current $150\,\mu A$ and ionisation energy 70 eV. The APTMS mass spectrum was presented in Fig. 2.

The argentometric determination of chloride ions concentration was performed using the potentiometer equipped with silver and calomel electrodes.

Determination of the concentrations enables performing the mass balance of each experiment and comparative evaluation by the calculation of CPTMS conversion and selectivity of transformation to APTMS. These values were calculated in the following way:

$$CPTMS\ conversion = \frac{amount\ of\ CPTMS\ consumed}{initial\ amount\ of\ CPTMS} \times 100\%$$

selectivity to APTMS in relation to consumed CPTMS

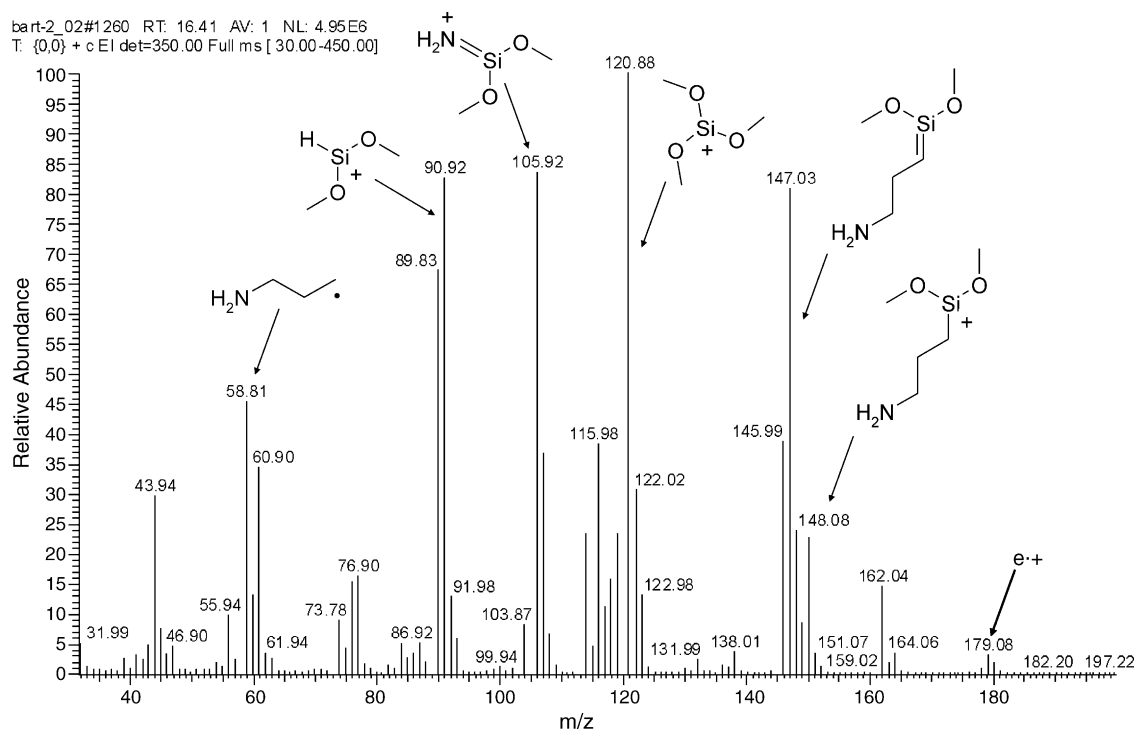$$= \frac{amount\ of\ APTMS\ obtained}{amount\ of\ CPTMS\ consumed} \times 100\%$$

Fig. 2. The mass spectrum of APTMS.

The amount of CPTMS consumed was calculated as a mean value from GC method and argentometry. The differences of the results between these two analytical methods not exceed 1.5%.

3. Results and discussion

The influence of temperature, reaction time and the molar ratio of NH_3/CPTMS on the selectivity of transformation to APTMS in relation to consumed CPTMS and on the conversion of CPTMS were investigated. The ranges of changes of studied parameters were assumed on the basis of the literature data [6,7].

3.1. Influence of the reaction time

A series of syntheses was performed in order to determine the influence of the reaction time on the course of the ammonolysis process. Each experiment was carried out two times at a temperature of 60 °C with the molar ratio of the NH_3/CPTMS 60:1, varying the reaction time in the range from 4 to 12 h. The experimental results are shown in Fig. 3.

The conversion of CPTMS is high over the whole range of reaction time used. This is in accordance with the theoretical assumptions. The aliphatic chloroderivatives readily undergo the reaction with ammonia to form the mixture of amines. The CPTMS conversion after 4 h was 85 mol%, whereas the total conversion of CPTMS (100 mol%) was achieved after at least 8 h. The selectivity of transformation to APTMS was 48 mol% after 4 h and reaches the values close to a minimum ~32 mol% after the reaction time of 6 h. The selectivity decrease is associated with the formation of by-products: amines of higher

orders, silanols, siloxanes and polymers. The high selectivity of transformation to APTMS was the most important value in this process, more important than conversion of CPTMS. Unreacted CPTMS can be recovered by distillation of the raw product and recirculated to the reactor. Increasing the CPTMS conversion results in the decrease of the selectivity of transformation to APTMS and in the increase of the final amount of the by-products. The experimental results shown that the highest selectivity 50 mol% can be achieved by shortening the reaction time to 4 h, however the CPTMS conversion decreases to 84 mol%. The reaction time of 4 h is the most favourable for the high yield of APTMS synthesis.
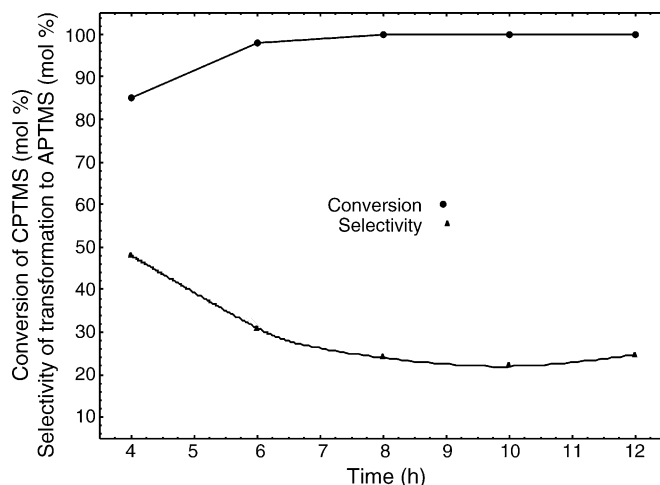

Fig. 3. Influence of the reaction time, temperature 60 °C, NH_3/CPTMS molar ratio 60:1.
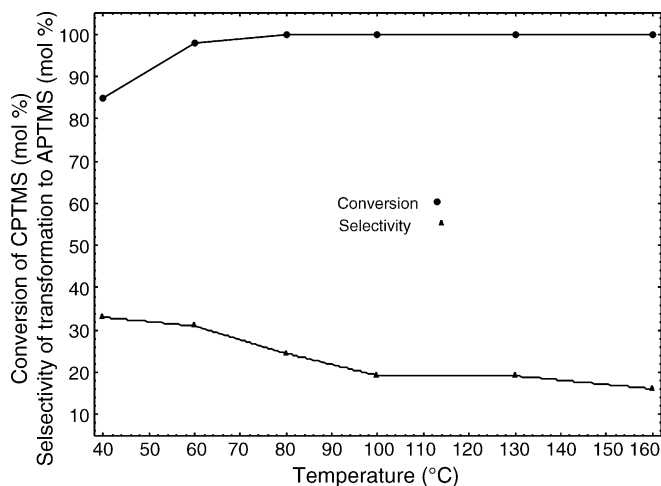
Fig. 4. Influence of the temperature, reaction time 6 h, NH$_3$/CPTMS molar ratio 60:1.

Fig. 5. Influence of the molar ratio of NH$_3$/CPTMS, temperature 60 °C, reaction time 6 h.

3.2. Influence of temperature

In order to determine the influence of temperature on the course of CPTMS ammonolysis its value was varied in the range from 40 to 160 °C. A series of syntheses was performed under the following conditions: the molar ratio NH$_3$/CPTMS = 60/1 and the reaction time 6 h. The experimental results are presented in Fig. 4.

The CPTMS conversion was high at the temperatures above of 60 °C. A 97 mol% conversion of CPTMS was achieved at temperature of 60 °C and 100 mol% above 80 °C. This means the possibility of temperature variations over a wide range. For this reason the selectivity is a decisive factor in the selection of process temperature. However at temperatures below 110 °C the majority of primary amines is durable in the hydrochloride form. The amine in the hydrochloride form is a more resistant for the alkylation by chloroderivative to the secondary and tertiary amines. This facilitates the achievement of higher selectivities of transformation to APTMS. After conducting these experiments it was found that the most advantageous temperature of ammonolysis is 60 °C.

3.3. Influence of the molar ratio NH$_3$/CPTMS

The influence of this parameter on the course of ammonolysis process was studied under the following conditions: reaction time 6 h, temperature 60 °C. The molar ratio of NH$_3$/CPTMS was varied in the range of 20–100 mol/mol by steps of 20 mol. The experimental results are shown in Fig. 5.

The selectivity of transformation to APTMS is significantly affected by a change of the molar ratio NH$_3$/CPTMS. However,
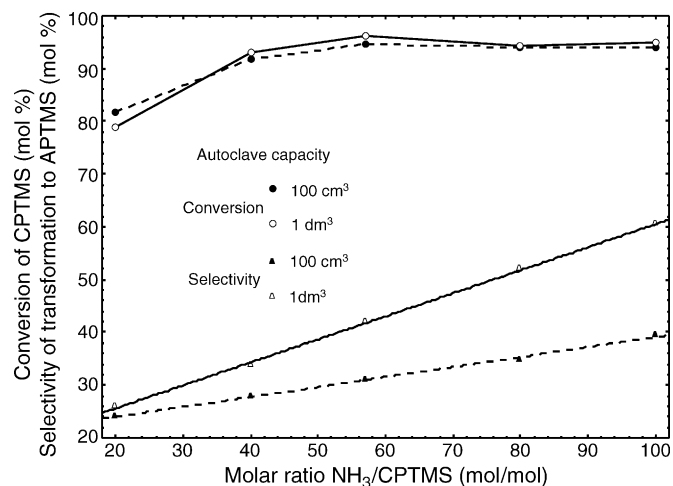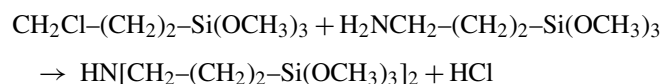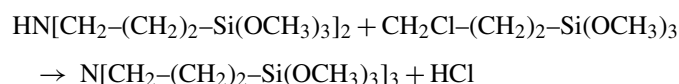
the CPTMS conversion changes less significantly. A large excess of ammonia decreases the contribution of alkylation reactions by the primary amines, according to the reaction:

$$CH_2Cl–(CH_2)_2–Si(OCH_3)_3 + H_2NCH_2–(CH_2)_2–Si(OCH_3)_3$$
$$\rightarrow HN[CH_2–(CH_2)_2–Si(OCH_3)_3]_2 + HCl$$

and in the case of secondary amines:

$$HN[CH_2–(CH_2)_2–Si(OCH_3)_3]_2 + CH_2Cl–(CH_2)_2–Si(OCH_3)_3$$
$$\rightarrow N[CH_2–(CH_2)_2–Si(OCH_3)_3]_3 + HCl$$

The CPTMS conversion does not undergo a change above the molar ratio of NH$_3$/CPTMS of 60/1. The selectivity increases linearly with increasing the molar ratio of NH$_3$/CPTMS. The increase of the selectivity is higher in the reactor with 1 dm^3 capacity. A reason of increase selectivity can be associated with larger losses of raw materials and the product during the synthesis performed on a small scale (100 cm^3). These losses are caused by the exceptional facility hydrolysis of both CPTMS and APTMS to silanols during a contact with humidity in the environment. In the autoclave with 1 dm^3 capacity this contact is smaller. Moreover, these compounds are also consumed in other side reactions such as the condensation of the raw material with silanols.

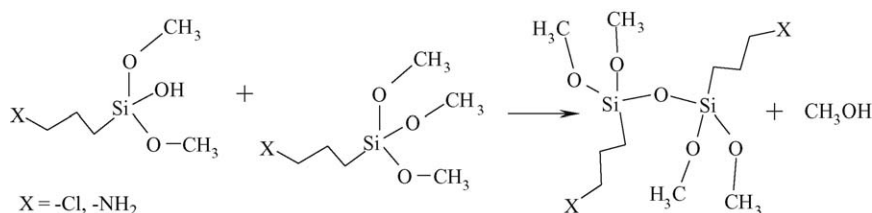The side reactions decreasing the selectivity of transformation to APTMS are proposed below:

• elimination:
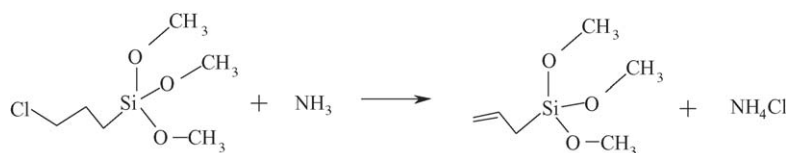
- hydrolysis of silyloalkoxy—the functional group in CPTMS and APTMS:
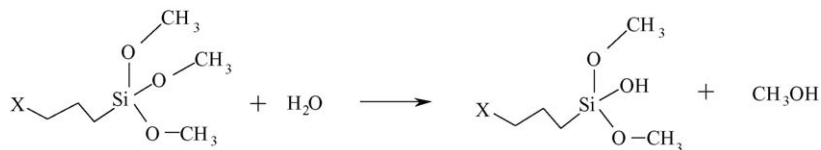
- the silanols are next condensed into siloxanes:

X = -Cl, -NH₂

In the presence of the water originating from the environment, both the long siloxane chains with the branched structure as well as the cyclic oligomers are formed as a result of the condensation.

The presence of methanol was found in each GC analysis after the application of propylbenzene as an extractant.

4. Conclusions

The performed investigations have demonstrated that the ammonolysis of CPTMS to APTMS proceeds under relatively mild conditions: temperature 60 °C, molar ratio NH₃/CPTMS 100/1 and reaction time 4 h. A prolongation of the reaction time and increase of temperature above 60 °C decreases the selectivity of transformation to APTMS. The most significant technological parameter influencing on the selectivity of transformation to APTMS is the molar ratio of NH₃/CPTMS. The selectivity of transformation to APTMS at given conditions is about 40 mol% and conversion of CPTMS is 97 mol% in the autoclave with 100 cm³ capacity. The selectivity to APTMS at the same conditions but in the autoclave capacity of 1 dm³ is about 60 mol%. The use of a larger excess of ammonia allows the preparation of the primary amine with a high yield and is cost-effective since ammonia can be readily recycled to the process.

The process does not require the application of high pressures. Under the given conditions of temperature and the molar ratio of raw materials the pressure was 1.7–2.5 MPa. The maintenance of the absolutely anhydrous reaction medium is important for preventing the hydrolysis of CPTMS and the products. The products of hydrolysis undergo both the condensation and polymerization and a white precipitate is formed.

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