High-selective catalytic systems based on derivatives of imidazole for the reaction of low-temperature disproportionation of trichlorosilane

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Abstract. The variety of catalysts based on macroporous supported ionic liquid-like phases using chloromethylsterene cross-linked with divinylbenzene (CMS / DVB) and different imidazolium cations was investigated in the disproportion of trichlorosilane. All samples were carefully characterized by the use of SEM, AFM, and nitrogen physisorption methods. The catalytic activity of different catalytic systems based on the macroporous support with different imidazolium functional groups was studied by the static method.

1. Introduction

Production of electronic-grade polysilicon (9N) by thermal decomposition of silane (SiH₄) is attracting greater interest, since it entails lower investment and low energy consumption costs, with minimal environmental pollution during production [1]. In addition, this silane has wide applications in optoelectronics, as well as micro- and nano-electronics for use in solar cells, and the semiconductor industry [2].

The silane mainly produced by the catalytic disproportionation of trichlorosilane (TCS) [2-4], decomposition of magnesium silicide and various modifications thereof [5-8], a method by plasma [9-11]. The method of the TCS disproportionation involves a simple process with a lower cost and high industrial safety, compared with the method based on the decomposition of magnesium silicide.

The production of silane (MS) by the TCS disproportionation primarily includes three major reversible reactions equations:

\[ 2\text{SiH}_2\text{Cl}_3 \Leftrightarrow \text{SiH}_2\text{Cl}_2 + \text{SiCl}_4 \]  
\[ 2\text{SiH}_2\text{Cl}_2 \Leftrightarrow \text{SiHCl}_3 + \text{SiH}_2\text{Cl} \]  
\[ 2\text{SiH}_3\text{Cl} \Leftrightarrow \text{SiH}_4 + \text{SiH}_2\text{Cl}_2 \]

The velocity of the TCS disproportionation can be increased by catalysis. There are several types of catalysts such as Lewis acids and acyclic nitriles [12-16]. However, almost all of them are a source of impurities in the products. The usage of organic homogeneous catalysts containing a nitrogen atom as a donor of an electron pair leads to challenging separations of products from the reaction mixture. Among the variety of organic and inorganic compounds which may catalyze the TCS disproportionation, special interest has been given to an anion exchange resin using chemically-inert matrices with a variety of functional groups and large specific surface areas [17].

Nowadays the most reputable catalyst from ion exchange resins (IER) for the TCS catalytic disproportionation were resins based on styrene-divinylbenzene (ST/DVB), containing functional groups strongly basic and weak ammonium groups in the form of chlorine. The most commonly used process for TCS catalytic disproportionation uses Amberlyst™ A-21 Dry and Amberlite® IRA-400
[18, 19]. The main disadvantage of its use is its poor thermal stability, which is limited to 100 °C; hence limiting the possibilities of the kinetic reactions (1) to (3) [20, 21].

Therefore, today one of the main scientific problems is the design of nanomaterials for catalytic technologies, able to intensify the key technological processes. Knowledge of the materials functioning at the nanoscale will allow solving a variety of problems: an improvement of the existing technologies, increasing the efficiency of the solar energy, an improvement of the selectivity and activity of catalysts.

These results have inspired the current study of catalytic properties with different physical and chemical parameters in the reaction of the TCS disproportionation.

2. Experimental

2.1. Materials
1-Methylimidazole and 4(5)-methylimidazole, divinylbenzene (DVB), chloromethylstyrene (CMS) were purchased from Sigma-Aldrich (Germany). Imidazole and 2-methylimidazole were purchased from Tomsk Special Forces Reagent Facility Ltd. (Russia). For disproportionation TCS we used as the initial substances: trichlorosilane (99.998%) from Firm HORST Ltd. (Russia).

2.2. Preparation and functionalization catalyst
DVB/CMS copolymer beads were obtained by suspension radical copolymerization [22, 23] of 4 ml DVB (33 % crosslinked agent) and 8 ml CMS along with 6 ml toluene and 6 ml heptane as porogens in 0.55% NaCl, 2.75% PVA (w/w) water solution (0.13 g of AIBN was used to initiate the reaction). At the first stage, a mixture of organic and water phases mixing up to 45 min in an ultrasonic bath. At the second stage, organic and water phases were mixed under overhead stirring (300 rpm) at 80 °C for 12 hours. After 12 hours product was trice washed with hot water and twice with ethanol to remove PVA from its surface, then other impurities, porogens, and unreacted monomers were extracted using Soxhlet apparatus (2 days in ethanol). After extraction polymer beads were dried in the vacuum oven for 1 day at 110 °C.

Functionalized polymer was obtained by reaction of initial DVB/CMS beads with five equivalents (methylene chloride groups content was calculated on the assumption that DVB and CMS reacted in 1:4 ratio) of corresponding imidazole derivative (or imidazole itself) in an appropriate solvent under mild stirring and heating (80 °C, 48 hours). The excess of imidazole or its derivative was removed by extraction using Soxhlet apparatus (ethanol, 1 day).

2.3. Static method for evaluating catalytic activity
The static method was chosen for determination of the catalytic activity of the catalysts in the disproportionation reaction of TCS. The apparatus was consisted of maintaining a mixture of TCS and helium in a thermostatically controlled reactor filled with the catalyst.

The experimental setup is shown in [21]. All lines of the experimental setup have a heated braid (temperature 60 °C), which prevents the condensation of chlorosilanes in gas lines. Gas mixture was supplied to the reactor with a catalyst (catalyst weight = 0.4 g), after which it was cut off from the vacuum system and allowed to set for one hour at a temperature of 373 K. Then the gas mixture from the reactor was quantified analyzed by GCMS at the moment when steady-state conditions and thermodynamic equilibrium were achieved (The experiment was repeated until the results converged, on average, no more than 3 times).

2.4. Characterization SILLPs
2.4.1 SEM, SEM-EDS mapping, AFM. The morphological and visual appearance characteristics were observed by scanning electron microscopy Vega II (Tescan, Czech Republic) at the voltage of 20 kV with backscattered electron (BSE) detector and detector of reflected electrons (RE detector) with
different zooming from. The use of BSE and RE detectors produces higher-contrast images in comparison to the SE detector.

The observation of energy dispersive spectroscopy (EDS) analysis (C, N and Cl mapping) and fracture surfaces, which were prepared under the aid of liquid nitrogen, of the hybrids were performed by the scanning electron microscopy JSM-6700F (JEOL, Japan). EDS mapping was carried out to characterize the elemental distribution of the samples.

The surface structure of the microspheres was studied by a scanning probe microscope SPM-9700 (Shimadzu, Japan). A maximal lateral scan area of AFM piezoelectric scanner was 30μm×30μm. The scans were data arrays with a dimension of 256×256 pixels. The probe sensitivity and the scanner accuracy of the atomic force microscope allowed to obtain surface images with a lateral resolution to 0.2 nm and a vertical resolution to 0.01 nm. Approximation levels were 30 μm, 10 μm and 3 μm. For checking purposes of reproducibility, the samples were scanned on different sites of their surface. The experiments were carried out under ambient conditions. To eliminate possible crosstalk artifacts (image defects due to crosstalk scanner), software corrective filters were used. In addition, automatic correction of linear noise during scanning.

2.4.2 Specific surface area and pore size distribution. Specific surface area and pore size distribution were determined from absorption/desorption isotherms recorded on SorbiMS (META, Russia) with advanced term training of samples. The study of solids is closely related to the interpretation of the IV type of adsorption isotherms, where there is a hysteresis loop. By interpreting this type of isotherms, it is possible to estimate the specific surface area by BET and STSA with acceptable accuracy, as well as to obtain an approximate characteristic of pore size distribution and full pore volume.

2.4.3 GCMS qualitative analysis. «Ex-situ» qualitative analysis of the major reaction products was carried out on GCMS – QP2010Plus (Shimadzu, Japan) with a vacuum sample inlet system through automatic injection valve (Valco Instruments Co Inc, USA). The products which were obtained in the reaction were separated on the Restek capillary column Rtx-200 (60 m, 0.25 mmID, film 1.0 um) with a stationary phase based on crossbond trifluoropropylmethyl polysiloxane at 323 K for 15 min; carrier gas – helium. Reaction products were identified with the help of NIST-11 database of mass spectra.

3. Results and discussion

3.1. Synthesis and characterization

In suspension polymerization, the size of the initial emulsion droplets depends on the balance between the droplet break-up and coalescence, which in turn is controlled by the type and speed of agitation used. For enhancing the agitation, the ultrasonic dispersion was employed and accurate (experimentally established) time intervals.

The size distribution of the obtained polymer beads has a maximum between 0.2 and 0.5 mm. They have a porous structure with incorporated hollow bubbles which have a diameter of 2-4 μm as can be seen on obtained SEM images in figure 1. Pores with a diameter of dozens and hundreds of nanometers were formed during polymerization due to soaking of growing polymer chain by toluene. And the hollow bubbles were formed due to phase separation of heptane which is bad solvent for polystyrene and derivatives from toluene-CMS-DVB-polymer chain system as polymer phase fraction grows. As it can be expected these hollow bubbles have a quite narrow size distribution as growing heptane drops are separated from each other by polymer chains during polymerization. Narrow beads size distribution can be explained by the effect of ultrasonic treatment as it stirs the monomer drops and provides even distribution of nascent chains at early stages of the polymerization by tearing up polymer chains larger than some length that is determined by the power of ultrasonic emitter and the composition of sonic wave medium.
Figure 1. SEM images of 4-MeImd catalyst (a - external structure, b - internal structure)

Mesoporous supports have advantages over micro- and macroporous ones. The specific surface area increases as the diameter of pores become smaller so support with the same mass but pore with a smaller diameter will have greater specific surface area. But as the pore diameter becomes smaller the gas transport properties of support worsen due to increase in flow resistance. So, mesoporous supports are a compromise between the specific surface area size and gas transport characteristics of support.

We used two measurement methods (BET and STSA) as BET method allows to measure micropores and mesopores using mono-layer model and STSA (or t-plot) method is appropriate to calculate mesopores, macropores and outside surface specific surface area (but not micropores one as micropores are already field in the range of relative pressures from 0.1 to 0.5 in which STSA operates) using multi-layer model [24]. So, for resins containing predominantly mesopores and macropores STSA specific surface area is always greater than BET one. As it is shown in table 1 our resins have mesoporous and macroporous morphology. The decrease in the specific surface area (both BET and STSA) and in the difference between measurements by BET and STSA methods allows concluding that during functionalization the smallest pores were closed or filled as polar imidazolium fragments draw support chains inwards and make removal of solvent harder. The decrease in the specific surface area becomes the most obvious in the case of 1-MeImdCl. It can be attributed to condensation of an excess of 1-methylimidazole in the pores smaller than several nanometers. As for the decrease in the proportion of pores with a diameter of 14 nm to cumulative pore volume, it should be mentioned that our equipment allows measuring pore volume only of pores with a diameter less than 100 nm. So, while micropores are closed or filled as a result of functionalization, some macropores also become smaller and available for pore volume measurement by our equipment. Increase in the dV_{14nm}/V_sum ratio in the case of 4-MeImdHCl can be rationalized by assuming that at the functionalization step non-polar 4-methylimidazole molecules have a greater affinity to the polymer chain and are more liable to close micropores than constrict macropores.
Table 1. Loading of the functional fragment (FF) and textural properties of the SILLPs.

| Entry | SIILLPs / FF | $S^BET$ (m$^2$/g) | $S^{STSA}$ (m$^2$/g) | Cumulative pore volume (cm$^3$/g) | $dV_{14nm}/V_{sum}$ (%) |
|-------|--------------|-------------------|----------------------|----------------------------------|--------------------------|
| 1     | Porous support | 70.0              | 85.4                 | 0.223                            | 39.9                     |
| 2     | PS / ImdH$^+$Cl$^-$ | 64.9              | 73.2                 | 0.211                            | 35.9                     |
| 3     | PS / 1-MeImd$^+$Cl$^-$ | 40.8              | 34.9                 | 0.180                            | 37.1                     |
| 4     | PS / 2-MeImdH$^+$Cl$^-$ | 63.1              | 70.3                 | 0.219                            | 35.8                     |
| 5     | PS / 4-MeImdH$^+$Cl$^-$ | 61.4              | 64.4                 | 0.215                            | 46.7                     |

In all cases, the functionalization was successful, the imidazole molecules were fixed on the polymer support by chemical bonding. In most cases, the effect of functionalization on the morphological properties of the carrier is negligible, but in the case of 1-methylimidazole, the decrease in the specific surface can be attributed to the condensation of 1-methylimidazole (this liquid) in the micropores of the polymer.

From the desorption isotherm, the pore size distribution was obtained. The results indicate that a different ratio of monomers to porogen affects the pore diameter and, as a consequence, the specific surface area. Figure 2 shows the distribution of pores (for a sample with 100% addition of porogen as an example), whose character is described by the Gaussian distribution with a maximum of 15 nm. The final results are shown in table 1.

![Figure 2](image)

**Figure 2.** Pore size distribution (a - full pore size distribution, b - pore size distribution of relative total volume).

The topography map shows the microsphere surface has a loose structure with pronounced large-scale relief in figure 3. According to AFM scanning, an arithmetic average roughness height (Ra) and a mean roughness depth (Rz) were obtained. A base length (a length of a line used for roughness selection) was 3 μm. Since the function of heights distribution (according to surface profile) is unimodal, Ra and Rz could be used as quantitative parameters of the surface irregularities. Wherein Ra correlates with an amplitude of the small-scale roughness, and Rz correlates with the large-scale one. From the results of the AFM analysis, Ra is about 20 nm, and Rz is about 100 nm.
Figure 3. AFM images of the microsphere surface and deflection map.

The deflection map shows numerous dark areas, i.e., those with the lowest heights. They were interpreted as pores. The pores had the shapes of conical capillaries. Their lateral sizes were determined by the surface micro profiles using the AFM software tools. The pore size was varied from 40 to 70 nm. With this pore size, the use of the chosen cantilever ruled out the effect of the contraction of profile valleys.

For determining the elemental distribution of the product, EDS mappings were carried out. Figure 4 displays SEM image of a single loop structure. The corresponding elemental mappings for C, Cl and N are exhibited in figure 4 a, b and c, respectively.

Figure 4. EDS mapping (a – element C, b – element Cl and c – element N).

The intensity of the corresponding lines indicates a uniform distribution of the active sites.
3.2 Catalytic activity
In this paper, we investigated the catalytic activity of the resulting immobilized ionic liquids under static conditions to determine which of them has the highest conversion and yield of MS.

As can be seen from table 2, the immobilized ionic liquid based on 4-methylimidazole showed the highest yield of MS and the highest conversion among the ionic liquids studied. The next most effective is the catalyst based on imidazole. Since the experiment was carried out under conditions of lack of TCS relative to the number of catalytic sites, a significant amount of reagents and products were not desorbed and, accordingly, not reflected in the results. Other products were monochlorosilane (MCS) and dichlorosilane (DCS). The study is of a qualitative nature, and its purpose is to determine the most promising catalyst.

Table 2. The catalytic activity of the different SILLPs catalysts.

| SILLPs / FF         | MS m/z 30 (%) | MCS m/z 64 (%) | DCS m/z 99 (%) | TCS m/z 133 (%) | STC m/z 170 (%) |
|---------------------|---------------|----------------|----------------|-----------------|----------------|
| Porous support      | -             | -              | -              | 98.42           | 1.58           |
| PS / Imd'Cl         | 0.61          | -              | -              | 39.07           | 60.31          |
| PS / 1-MelImd'Cl    | 0.01          | -              | 0.02           | 53.58           | 46.39          |
| PS / 2-MelImd'Cl    | 0.04          | 0.10           | -              | 48.92           | 50.95          |
| PS / 4-MelImd'Cl    | 2.26          | -              | -              | 39.98           | 57.76          |

Taking into account that the maximum theoretical yield of MS is 4.5%, the results obtained in the static method of determining catalytic activity are quite promising, therefore, in the future work, a catalyst based on 4-methylimidazole will be investigated for kinetic studies, since it has the largest catalytic activity among the samples studied.

4. Conclusion
A method for the synthesis of polymer substrates for a catalyst was developed and their functionalization by various imidazole derivatives was carried out. SEM images of the cleaved microspheres in figure 1b demonstrate a homogeneous porous structure, which is confirmed using an x-ray microanalysis in the "mapping" mode EDS map) over the active centers in figure 4c. The transverse dimensions of the pores were determined and statistical processing of the data was carried out. The immobilized ionic liquid based on 4-methylimidazole showed the highest yield of monosilane and the highest conversion among the investigated ionic liquids.

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5. References
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