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Organosilicas with Covalently Bonded Groups under Thermochemical Treatment

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Silica-based hybrid materials having covalently immobilized vinyl ($SiO_2-C_2H_3$), chloropropyl (SiO_2-R-Cl), trimethylsilyl (SiO_2-SiMe_3), ethyl sulfonic acid (SiO_2-R-SO_3H), and aminopropyl (SiO_2-R-NH_2) groups, as well as the salt of the latter with HNO_3 ($SiO_2-R-NH_2{\cdot}HNO_3$) were studied by different thermoanalytical methods: thermogravimetry (TGA), differential thermal analysis (DTA), and temperature-programmed desorption mass spectrometry (TDP-MS). It was demonstrated that TPD MS can be successfully used for the investigation of the interfacial layer in such materials. Particularly, it was shown that a side reaction between the grafted group and aromatic solvents is possible during the preparation of $SiO_2-C_2H_3$ and SiO_2-R-Cl. For SiO_2-SO_3H the formation of 2-Si-ethanesulfonic, 1-Si-ethanesulfonic, and 2,4-Si-butanesulfonic acid grafted groups with the predominance of the 2-Si isomer was found. The process of $SiO_2-NH_2{\cdot}HNO_3$ decomposition at 500 K may be applied for the preparation of silica modified by aldehyde groups. Mechanisms of thermal transformations of bonded layer were established and the key role of the reactions of grafted groups with silanols in such processes was demonstrated. As was found for SiO_2-R-Cl and SiO_2-R-NH_2, the decomposition process with participation of silanols is realized in two stages. The first one occurs in the 400−700 K range and includes the interaction between organic groups and the neighboring silanol. The second decomposition stage occurs above 700 K and includes migration of the bonded groups on the silica surface.

I. Introduction

Porous silicas having an immobilized organic layer (chemically modified silicas, CMS) are widely used as adsorbents,[1] chromatography phases,[2,3] and catalysts.[4,5] Useful properties of such hybrid materials are determined by the chemical nature of their interfacial layer and particularly by its composition,[6−8] geometry,[9] and topography (microheterogeneity).[10,11] Certainly, the composition of the immobilized layer is most crucial. Only in the simplest cases (for CMS obtained in one-step immobilization reaction) the composition of the surface layer can be determined from CMS chemical analysis.[11] Most of the CMS can only be synthesized by the multistage chemical transformations of the organic groups grafted on the silica surface (this is so-called surface assembling method). In such transformations the conversion of one grafted group to another commonly has a low yield.[11] Thus, the interfacial layer for most CMS has a multifunctional nature and its composition cannot be determined from the results of CMS chemical analysis. Spectral methods such as FTIR or MAS NMR have their own limitations if used for qualitative analysis of the CMS grafted layer. Many characteristic FTIR bands of the organic groups are located in the region of SiO_2 absorbance. Strong signals of water, adsorbed on the silica surface at ambient conditions, usually cover completely the signals of organic fragments in FTIR and ^1H MAS NMR spectra. That is why experiments on FTIR and ^1H MAS NMR of CMS require special precautions to avoid the contact of sample with water vapors.

The method of mass spectroscopy is one of high selectivity and sensitivity, making it attractive for the characterization of materials with functionalized surfaces. For qualitative analysis of the immobilized layer composition, temperature-

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Scheme 1. Silanization Reaction

$$m\ SiO_2)\text{-}OH + X_nSiR_{4-n} = SiO_2)\text{-}O\}_m\text{-}SiX_{n-m}R_{4-n} + HX$$
$$\text{on air: } \equiv Si\text{-}X + H_2O = \equiv Si\text{-}OH + HX$$
$$n = 1\text{-}3;\ m \leq n;\ X = \text{Hal, -OR, } etc.$$

programmed desorption mass spectrometry (TPD-MS) proved to be useful.[12] TPD-MS was successfully applied in the study of carbosils[13] and silica gels with grafted alcoxy[14] and aminoalkyl[15,16] groups.

The aim of the present work is to demonstrate the potential of TPD-MS in the investigation of the interfacial layer composition for organosilicas having covalently immobilized groups, including those where the immobilized layer has a multifunctional nature. We also tried to determine the general peculiarities in the thermal decomposition pathways of such CMS. For the investigation chromatographically important CMS were selected: silica gel with immobilized vinyl (**$SiO_2-C_2H_3$**), chloropropyl (**SiO_2-R-Cl**), trimethylsilyl (**SiO_2-SiMe_3**), and aminopropyl (**SiO_2-R-NH_2**) groups. Nitrate salt of aminopropyl silica (**$SiO_2-R-NH_2\cdot HNO_3$**) was also studied. In addition, new potentially catalytically important silica with immobilized ethylsulfonic acid (**SiO_2-R-SO_3H**)[17] was analyzed. Methods of thermogravimetry (TGA) and differential thermal analysis (DTA) were used in addition to TPD-MS for the examination of the bonded layer composition, establishing of decomposition mechanisms, and determination of organic loading.[18-20]

II. Experimental Section

II.1. Materials. Silica gel with a surface area of 300 m^2/g and mean pore diameter of 6 nm (Lachema, Czech Republic) was used as the starting material for the syntheses of $SiO_2-C_2H_3$, SiO_2-R-Cl, and SiO_2-SiMe_3. Macroporous silica with a surface area of 80 m^2/g (silochrome C-80 from Stavropol Luminophore Plant, Russia) was used for preparation of SiO_2-R-NH_2. The materials listed above were prepared by a one-step silanization reaction, giving a monofunctional hydrolytically stable grafted layer (Scheme 1).

Before silanization the silanes were distilled and the silicas were annealed at 823 K for 8 h in air. To obtain a CMS, 1 g of bulk dry silica was stirred with 1 mmol (0.3 mmol for $(EtO)_3Si(CH_2)_3NH_2$) of silane in 10 mL of organic solvent at the elevated temperature. The resulting solid was washed on a glass filter by the solvent in which the synthesis was carried out, followed by acetonitrile in a Soxhlet extractor. The washed product was dried at 400 K in air and then in vacuum. The reaction conditions and the grafted group's concentrations are listed in Table 1.

Table 1. List of CMSs Obtained by Silanization Together with Silanes Used for This, Synthesis, Conditions, and Concentration (C_L) of Bonded Groups (μmol/g) Determined from Chemical Analysis and TGA

		reaction conditions				
sample ID	silane	solvent	T/K	t/h	C_L	C_L (TGA)
$SiO_2-C_2H_3$ (1)	$Cl_3Si-C_2H_3$	toluene	353	6	690	
$SiO_2-C_2H_3$ (2)		*o*-xylene	408	7	283	
$SiO_2-C_2H_3$ (3)		toluene	373	36	280	
SiO_2-R-Cl	$Cl_2Si(CH_3)(CH_2)_3Cl$	*o*-xylene	408	20	472	496
SiO_2-SiMe_3	$ClSi(CH_3)_3$	*o*-xylene	408	10	800	753
SiO_2-R-NH_2	$(EtO)_3Si(CH_2)_3NH_2$	toluene	373	8	180	180

Table 2. List of Some Characteristics of SiO_2-R-SO_3H Samples

sample ID	ID of the source	$C_L(SO_3H)$ (μmol·g)	$C_L(C_2H_3)$ (μmol·g)
SiO_2-R-SO_3H (1)	$SiO_2-C_2H_3$ (1)	302	235
SiO_2-R-SO_3H (2)	$SiO_2-C_2H_3$ (2)	102	103

One sample of vinyl-silica ($SiO_2-C_2H_3$ (1)) was prepared in the presence of water (1 mmol) and pyridine (5 mmol) in toluene. Such conditions for the silanization promote silane hydrolysis and further condensation prior to immobilization. This CMS has a "polymeric" structure of the grafted layer.[2] All other CMS were obtained under conditions preventing the hydrolysis of silane; they have a "monomeric" grafted layer.[2]

The SiO_2-R-SO_3H was obtained from $SiO_2-C_2H_3$ by a radical initiated addition of $NaHSO_3$ in 20% water solution at 343 K, as described previously.[17] Two samples of SiO_2-R-SO_3H having a high and low loading of immobilized ethylsulfonic acids were obtained, Table 2.

II.2. Methods of Characterization. The concentration of grafted acidic and basic groups (C_L) in SiO_2-R-SO_3H and SiO_2-R-NH_2, respectively, was determined by pH titration of those CMS in water suspension. The concentration of vinyl groups in $SiO_2-C_2H_3$ and SiO_2-R-SO_3H was determined by bromometric titration.[21] For SiO_2-R-Cl and SiO_2-SiMe_3 the concentration of grafted groups was determined from elemental analysis of chlorine and carbon, respectively. Additionally, the total concentration of grafted organic groups for several CMS was determined from DTA data. Assuming that the samples of bulk and modified silicas heated to 973 K have the same extent of surface hydroxylation, the following formula was used for the calculations

$$C_L = \frac{\dfrac{\Delta m_{473-973}(\text{sample})}{m(\text{sample})} - \dfrac{\Delta m_{473-973}(SiO_2)}{m(SiO_2)}}{M - 9 \times N}$$

where $\Delta m_{473-973}$(sample) is the mass loss of the experimental sample in the 473−973 K interval, m(sample) is the mass of the dried at 373 K sample, $\Delta m_{473-973}(SiO_2)$ and $m(SiO_2)$ are the corresponding values for the initial silica, pretreated before the synthesis at 823 K, M [g/mol] is the molecular weight of organic residues (R in Scheme 1), 9 [g/mol] is the molecular weight of 0.5 mol of H_2O, produced by elimination of one Si−OH group, and N is the number of silanols, which have been substituted by one silane molecule. The silane with general formula $XSiR_3$ was supposed to substitute one, with X_2SiR_2 two, and with X_3SiR one silanol. In the latter case formation of a $\{SiO_2)-O\}_2-Si(OH)R$ structure was assumed.

TPD-MS measurements were carried out by heating the CMS sample in high vacuum ($p < 10^{-3}$ Pa) with a heating rate of 0.167 K/s. The evolving products were analyzed by mass spectrometry

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on the instrument MX7304A (Selmi, Ukraine).[14] Before TPD-MS measurements the samples were evacuated to 10^{-3} Pa, for 20 min. Thermal analysis was performed on a Q-1500 Paulik−Paulik−Erdey instrument (Hungary) in air at atmospheric pressure with Al_2O_3 as a reference material and a 0.167 K/s heating rate. The diffuse reflection infrared spectra with Fourier transformation (DRIFT) were recorded on a Bruker Vector 22 instrument equipped with Harrick Scientific Praying Mantis diffuse reflection accessory. MAS NMR spectra were measured on a Varian UNITY/nova 300 MHz instrument with a MAS spinning rate of 4 kHz. Samples of CMS were dried at 400 K in a vacuum prior to any spectral measurements.

III. Results and Discussion

To evaluate the thermal stability of experimental CMS and to determine the overall loading of organics, the thermogravimetric method was used as described in refs 18−20. For all studied samples the mass loss at 300−450 K (Figure 1a,b) along with the endothermic effect in the DTA (Figure 1c) was observed. Commonly, the process of mass loss in this low-temperature region is attributed to desorption of physically adsorbed water.

In the higher temperature region (473−1073 K), unmodified silica gel loses its mass linearly with a broad endothermic effect (Figure 1). This mass loss is attributed to the elimination of water by condensation of surface silanols.[1]

In contrast to unmodified silica, CMS decompose at 473−973 K with stepwise processes of mass loss (Figure 1a,b) accompanied by strong exothermic effects in the DTA (Figure 1c). Since the decomposition of the bonded organic phase is the reason for those effects, the value of mass loss at 473−973 K can be used for the calculation of the total organic loading. The results of such calculations, presented in Table 1, show that TGA can be correctly used for determination of C_L only for CMS with a monofunctional immobilized layer: $SiO_2{-}R{-}Cl$, $SiO_2{-}SiMe_3$, and $SiO_2{-}R{-}NH_2$. For these CMS the data obtained are in good agreement with the data of their titration and elemental analysis.

To follow the desorption of water from bulk silica gel, ions with m/z 18 (H_2O^+) and 17 (OH^+) were monitored by TPD-MS. Figure 2 demonstrates the temperature profile of water desorption for silica preliminarily dried in vacuum at ambient temperature to remove physically adsorbed water. As can be seen from Figure 2, chemically bonded water is evolved from the silica surface in two steps. The maximum of water desorption observed at 500 K is due to the condensation of vicinal silanol groups.[22] The higher temperature maximum at 923 K is a result of condensation of isolated and geminal silanols. The reason for such a big difference in temperature for silanols dehydroxylation is as follows: the average distance between two isolated silanols (7 Å) is significantly larger than the Si−O−Si distance (2 × 1.63 Å).[22] Therefore, the condensation of isolated silanols is only possible if their migration along the silica surface, occurring as consecutive reactions between Si−OH and Si−O−Si groups, takes place. As can be seen from the H_2O desorption profile, such migration occurs at temperatures higher than 700 K.

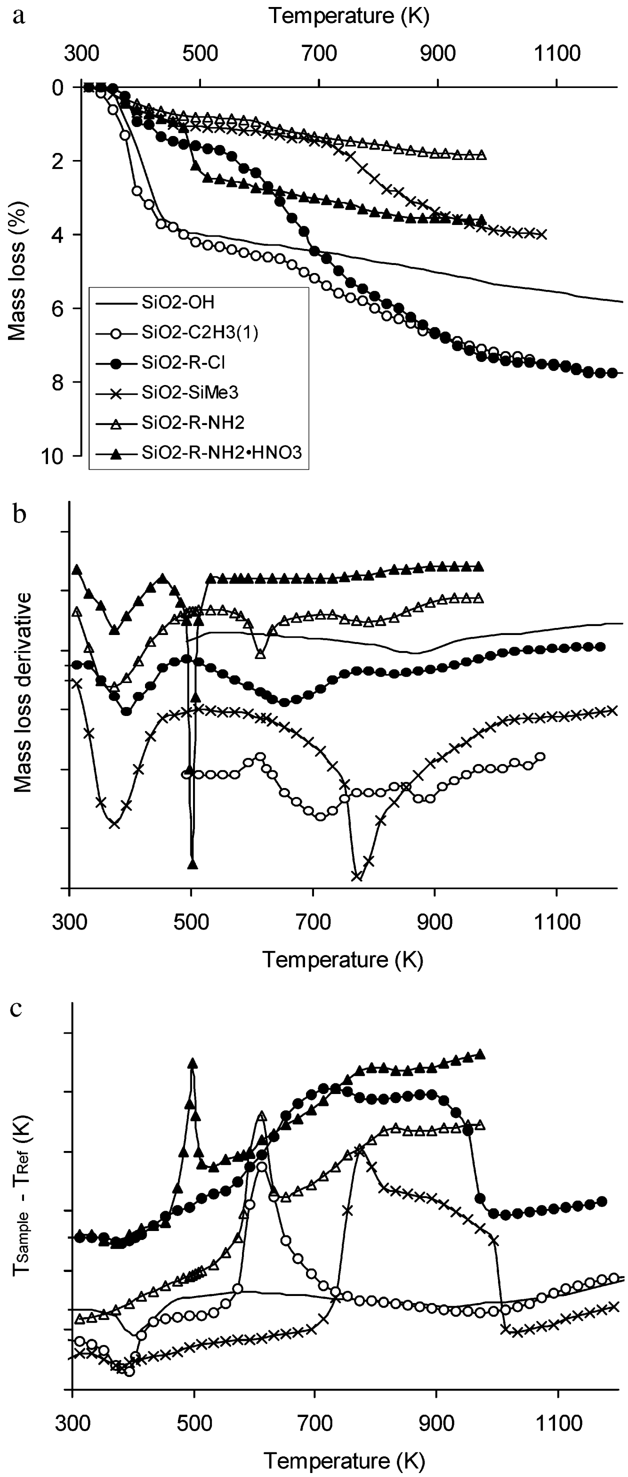

Figure 1. Results of the thermogravimetry and differential thermal analysis studies of the CMS: (a) thermogravimetry curves (TG); (b) derivative thermogravimetry curves (DTG); (c) differential thermal analysis curves (DTA).

The thermochemical behavior of silanols on a CMS surface was expected to be similar to that on bulk silica. Indeed, for all studied CMS, water formation from vicinal silanols was observed at 500−600 K (Figures 3−6). However, the high-temperature maximum of water evolution, associated with dehydroxylation of isolated silanols, is not observed for most of the studied CMS (see Figures 3 and 4, for example). This

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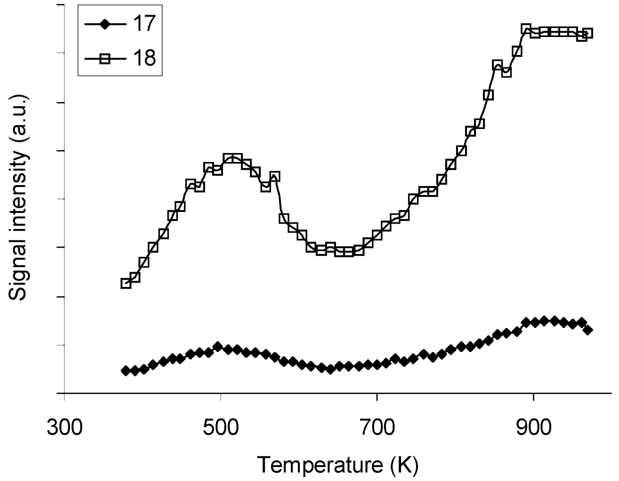


Figure 2. TPD-MS profiles of SiO_2-OH for the ions with *m*/*z* 17 (OH^+) and 18 (H_2O^+).

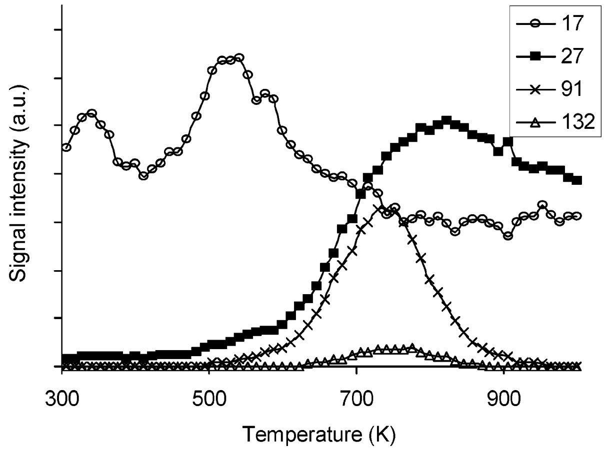


Figure 3. TPD-MS profiles of $SiO_2-C_2H_3$ (2) for the ions with *m*/*z* 17 (OH^+), 27 ($C_2H_3^+$), 91 ($C_7H_7^+$), and 132 ($C_{10}H_{12}^+$, dimethylstyrene).

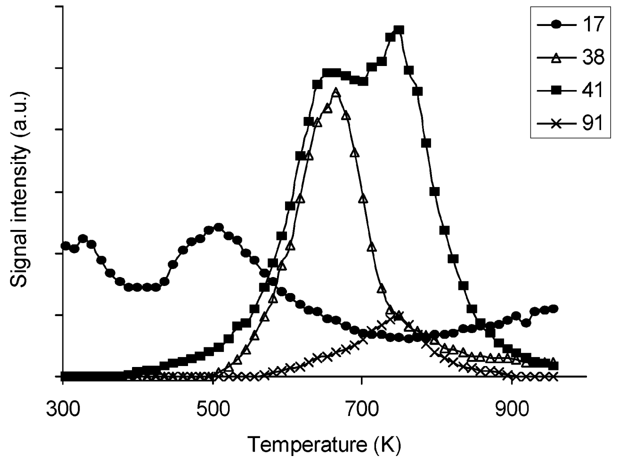


Figure 4. TPD-MS profiles of SiO_2-R-Cl for the ions with *m*/*z* 17 (OH^+), 38 ($H^{37}Cl^+$), 41 ($C_3H_5^+$), and 91 ($C_7H_7^+$).

observation is explained by consumption of isolated silanols during the silane immobilization (Scheme 1). Reaction of silanes with isolated silanols is confirmed by FTIR, for example.[11] Also, as will be concluded below, the silanols can be consumed during the decomposition of the CMS organic layer.

The thermal decomposition of the interfacial layer on $SiO_2-C_2H_3$ proceeds differently in air and in vacuum. In contrast to all other studied CMS, $SiO_2-C_2H_3$ in air has gained its mass by about 610 K, Figure 2. This effect may be explained by the addition reaction of oxygen to the double bonds of the grafted $-C_2H_3$ groups. A further increase of temperature (to 713 K) leads to decomposition of the immobilized organic layer and mass loss. In vacuum, $SiO_2-C_2H_3$ thermodegrades at 600−900 K, releasing ethylene, which is observed in the mass spectra as ions with *m*/*z* 28 (C_2H_4), 27 ($C_2H_3^+$), and 26 ($C_2H_2^+$) (Figure 3). Ethylene can form as the result of the reaction between immobilized vinyl groups and silanols, according to Scheme 2.

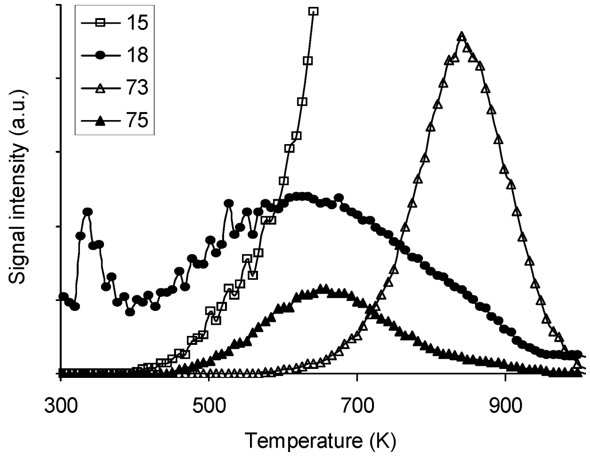


Figure 5. TPD-MS profiles of SiO_2-SiMe_3 for the ions with *m*/*z* 15 (CH_3^+), 18 (H_2O^+), 73 ($Si(CH_3)_3^+$), and 75 ($HOSi(CH_3)_2^+$).

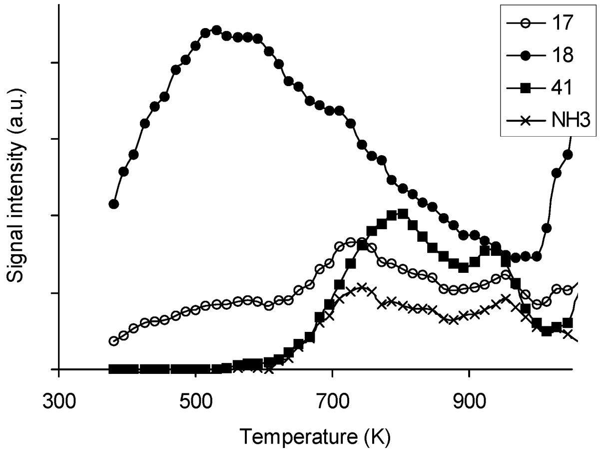
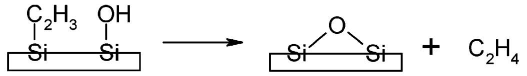


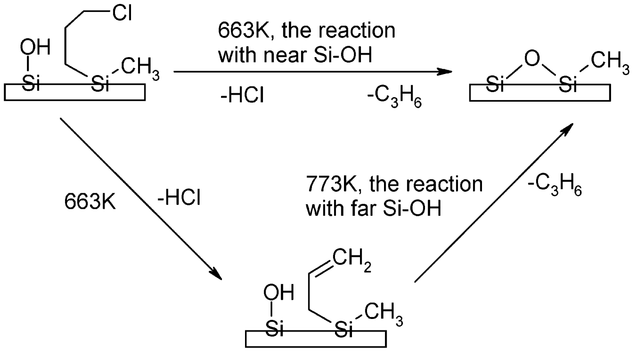
Figure 6. TPD-MS profiles of SiO_2-R-NH_2 for the ions with *m*/*z* 17 ($NH_3^+ + OH^+$), 18 (H_2O^+), and 41 ($C_3H_5^+$) and calculated intensity of the NH_3 signal.

Scheme 2. Thermal Decomposition of a Vinyl Group on SiO_2 Surface



The proposed scheme of bonded layer decomposition is in good agreement with the wide temperature range of ethylene evolution observed by TPD-MS. Indeed, the reaction illustrated by Scheme 2 includes intermolecular interaction between two neighboring surface groups and so strongly depends on the interfacial layer microstructure (distance and orientation of reacted bonded groups). In addition to ethylene, the formation of aromatic compounds (ions with *m*/*z* 132 ($C_{10}H_{12}^+$), 91 ($C_7H_7^+$), and others) was also detected in the TPD-MS of $SiO_2-C_2H_3$ (Figure 3).

Scheme 3. Pathways of Thermal Decomposition of Chloropropyl Groups



The thermal decomposition of SiO_2-R-Cl in air (Figure 1), as well as in vacuum, occurs in two steps (Figure 4). First, HCl (ions with m/z 36 ($H^{35}Cl^+$) and 38 ($H^{37}Cl^+$)) and C_3H_6 (ions with m/z 42 ($C_3H_6^+$) and 41 ($C_3H_5^+$)) simultaneously evolve at 663 K; second, at 773 K additional evolution of C_3H_6 occurs again (Figure 4).

It can be assumed that the low-temperature elimination of C_3H_6 takes place when immobilized organic groups are surrounded by silanols. If such a fine structure of the bonded layer is not achieved, then the thermal decomposition of immobilized organics takes place at higher temperature, when migration of surface silanols becomes possible. Since such migration is initiated at temperatures higher than 700 K (see above), the maximum intensity of high-temperature C_3H_6 desorption is observed at 773 K. Both thermochemical pathways of SiO_2-R-Cl decomposition can be presented by Scheme 3.

TPD-MS enables us to determine the specific features of $SiO_2-C_2H_3$ and SiO_2-R-Cl if they were prepared by SiO_2 silanization in anhydrous toluene or xylene (samples 2−4, Table 1). In the TPD-MS of these silicas, in addition to common fragments generated by immobilized vinyl and chloralkyl groups, other fragments that only can be assigned to the decomposition of aromatic compounds were found. These are as follows: dimethylstyrene (ions with m/z 132 ($C_{10}H_{12}^+$), 117, 106, and 91) for $SiO_2-C_2H_3$ (2), (Figure 3); methylstyrene (ions with m/z 118 ($C_9H_{10}^+$), 117, and 91) for $SiO_2-C_2H_3$ (3); and dimethylpropylenebenzene (ions with m/z 146 ($C_{11}H_{14}^+$), 132, 117, 105, and 91) for SiO_2-R-Cl (Figure 4). When $SiO_2-C_2H_3$ (2) was used as the starting material to prepare SiO_2-R-SO_3H (2), ions with the same masses were found in the TPD-MS of the last CMS (see Figure 7). The derivatives of toluene and xylene are evolved from CMS at 500−900 K in vacuum, so they cannot be assigned to physically adsorbed solvents since the temperature of desorption is too high. Instead, the chemical binding of toluene and xylene to the silica surface should be considered. That binding can take place due to a Friedel-Krafts reaction between toluene (or xylene) and an immobilized vinyl (or chloralkyl) group during CMS preparation or post-treatment, as is shown in Scheme 4.

The chlorosilanes used in excess for the preparation of $SiO_2-C_2H_3$ and SiO_2-R-Cl may act as a catalyst for this reaction. The side reaction of solvent (toluene and xylene) immobilization during silica silanization was confirmed by the DRIFT and MAS NMR spectra of the CMS. In the DRIFT spectra of $SiO_2-C_2H_3$ (2) in addition to bands at 3069, 3029, 2992, and 2965 cm^{-1} attributed to the ν(C−H) vibrations of the $-C_2H_3$ group, bands at 2927, 2890, 2860 cm^{-1} assigned to the ν(C−H) vibrations of alkyl groups were observed. A weak signal at 6.5 ppm in the ^1H MAS NMR spectra of SiO_2-R-Cl assigned to the protons in an aromatic ring also proved the side reaction of xylene immobilization. A sample of $SiO_2-C_2H_3$ (1) was synthesized in the presence of water, i.e., in conditions unfavorable for the Friedel-Krafts reaction. As was expected, aromatic fragments were observed neither in the TPD-MS nor in the FTIR spectrum of that sample.

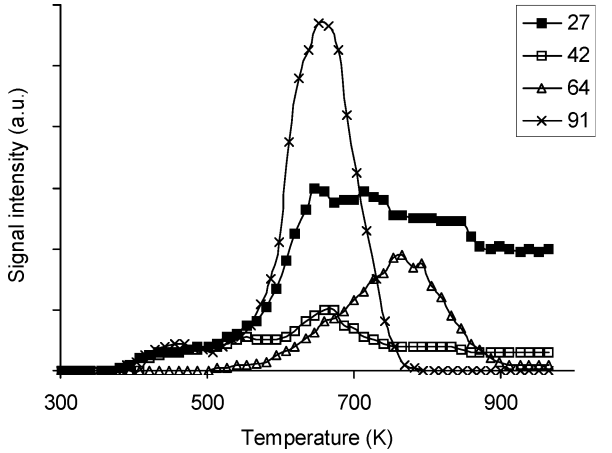
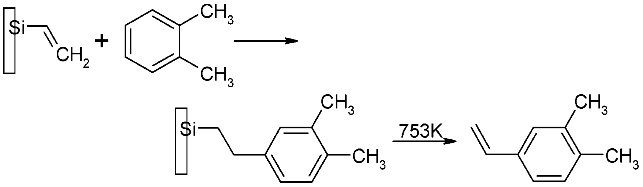


Figure 7. TPD-MS profiles of SiO_2-R-SO_3H (2) for the ions with m/z 27 ($C_2H_3^+$), 42 ($C_3H_6^+$), 64 (SO_2^+), and 91 ($C_7H_7^+$).

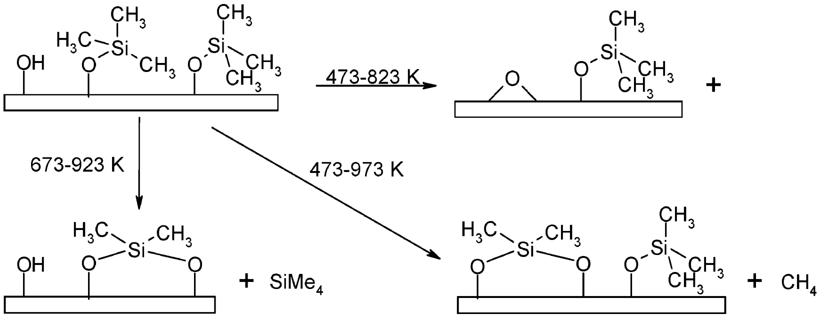
Scheme 4. Formation and Thermal Decomposition of Silica-Bonded Alkylaromatic Groups



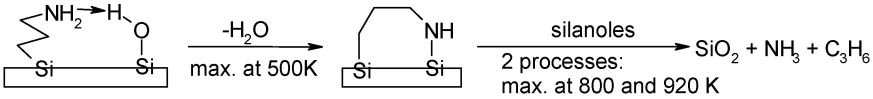
The DTA data show that SiO_2-SiMe_3 is stable to air oxidation up to 673 K (Figure 1b). Its stability in vacuum is about the same (Figure 5). From the TPD-MS data it can be concluded that the main fragments of SiO_2-SiMe_3 thermal degradation are as follows: CH_4 (ions with m/z 16 (CH_4^+), 15, and 14), $HO-Si(CH_3)_3$ (ions with m/z 90 ($HOSi(CH_3)_3^+$), 75 ($HOSi(CH_3)_2^+$), and 47), and $Si(CH_3)_4$ (ions with m/z 88 ($Si(CH_3)_4^+$), 73 ($Si(CH_3)_3^+$), and 45). Two main pathways were observed for SiO_2-SiMe_3 thermodecomposition: condensation of the bonded trimethylsilyl group with a neighboring silanol producing methane or $HOSiMe_3$, Scheme 5.

An additional minor pathway gives $SiMe_4$ as a product of SiO_2-SiMe_3 thermodecomposition. $SiMe_4$ can form as a result of condensation between two neighboring $-OSiMe_3$ groups (Scheme 5). This minor pathway can be explained by the high loading of trimethylsilyl groups on the SiO_2-SiMe_3 surface (see Table 1) and consequently by the low concentration of water and silanols in this CMS interfacial layer. Since migration of $-SiMe_3$ can be expected at higher temperatures, then −OH migration, the evolving of $SiMe_4$ (Scheme 5), should be expected at high temperature. Experi-

Scheme 5. Thermal Decomposition of Silica-Grafted Trimethylsilyl Groups



Scheme 6. Thermal Decomposition of an Aminopropyl Group



ment supports this assumption; the maximal intensity of $SiMe_4$ evolving during SiO_2-SiMe_3 thermal decomposition was observed at 860 K (Figure 5).

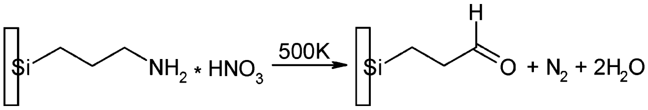
Two thermochemical processes were observed during the thermal decomposition of SiO_2-R-NH_2 in air. The first one occurs at 480−620 K and the second one at 723−873 K (Figure 1). The thermogravimetry method was used to calculate the mass loss for those processes. It was found that during the lower temperature process 18 g of a volatile compound is generated per 1 mol of immobilized amino groups. This mass loss may correspond to the formation of H_2O (18 g/mol) or NH_3 (17 g/mol) molecule. For further investigation of the SiO_2-R-NH_2 thermal decomposition mechanism, a TPD-MS experiment was used (Figure 6).

To interpret the TPD-MS data correctly, we considered that NH_3^+ and OH^+ ions have the same m/z 17 and cannot be distinguished by low-resolution mass spectrometry. But with use of the fact that the intensity of signal from OH^+ ion in the mass spectrum of water is 5 times lower than the intensity of H_2O^+ ion (m/z 18), the profile of NH_3 desorption can be obtained by subtraction of the OH ion signal (calculated as $0.2 \cdot I_{18}$) from the signal with m/z 17 (NH_3^+ and OH^+ ions). The results of a process, shown in Figure 6, demonstrate that under thermal treatment SiO_2-R-NH_2 simultaneously releases ammonia and C_3H_6. This occurs at temperatures higher than 700 K. The only volatile product forming at lower temperatures (480−620 K) is water. Therefore, the process of mass loss in the low-temperature interval can be presented by the condensation reaction between the silanol and amino group, as shown in Scheme 6.

The SiO_2-R-NH_2 decomposition at temperatures higher than 700 K has two maxima on the temperature scale. This effect can be explained in the same manner as was done for SiO_2-R-Cl: if silanols occur in the vicinity of the bonded molecules, the reaction of CMS thermal decomposition, leading to the elimination of organics, takes place at lower temperature; if not, silanol should migrate to initiate the reaction.

The thermal decomposition of $SiO_2-R-NH_2 \cdot HNO_3$ has the sharpest profile among any other studied CMS (Figure 1). At about 500 K, $SiO_2-R-NH_2 \cdot HNO_3$ has a quick mass loss process that is mirrored in its DTG as a sharp peak (Figure 1b) and gives a strong exothermic effect in the DTA (Figure 1c). Due to the oxidative ability of nitrate, the formation of aldehyde groups is proposed as a main pathway for $SiO_2-R-NH_2 \cdot HNO_3$ thermal transformation, Scheme 7.

Scheme 7. Thermal Decomposition of an Aminopropyl Group Nitrate



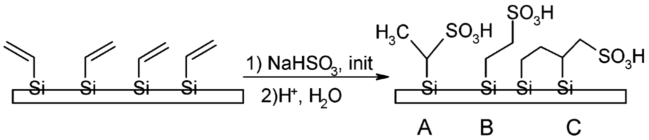
The proposed scheme is evidenced by the TG data. It was found that at 500 K the mass loss of $SiO_2-R-NH_2 \cdot HNO_3$ is about 64 g/1 mol of immobilized salt. This correctly corresponds to the formation of 2 mol of water and 1 mol of nitrogen as shown in Scheme 7.

Additional evidence for the formation of a silica-bonded alkylaldehyde (SiO_2-A) as the result of the $SiO_2-R-NH_2 \cdot HNO_3$ thermal transformation was obtained from DRIFT spectroscopy of SiO_2-A. The bands at 1520 and 1535 cm^{-1} found in $SiO_2-R-NH_2 \cdot HNO_3$ and assigned to δ(N−H) vibrations were absent in DRIFT spectra of SiO_2-A. Instead, a new band at 1735 cm^{-1} was developed. The latter band was assigned to a ν(C═O) vibration in an immobilized aldehyde. Also, SiO_2-A reacts with 2,4-dinitrophenylhydrazine (a reagent for functional analysis of aldehydes), giving a bright orange hydrazone.

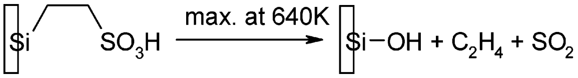
As was mentioned above, CMS obtained by the surface assembling method commonly have a multifunctional nature for the bonded layer.[11] SiO_2-R-SO_3H is an example of such a CMS. This CMS was obtained from $SiO_2-C_2H_3$ by hydrosulfite addition to the carbon−carbon double bond. As a result of this free-radical reaction, an immobilized layer with a mixture of different alkylsulfonic acid groups and residual vinyl groups is formed on the SiO_2-R-SO_3H surface, Scheme 8.[17]

In the DRIFT spectrum of SiO_2-R-SO_3H (1), bands at 2934, 2914, and 2858 cm^{-1} assigned to ν(C−H) vibrations of CH_2 fragments in 2-Si-ethanesulfonic acid (**B** structure in Scheme 8) were found. However, no absorption bands were observed at 2872 cm^{-1}, in the region of the $-CH_3$ characteristic vibrations. This indicates a low contribution

Scheme 8. Synthesis of SiO_2-R-SO_3H



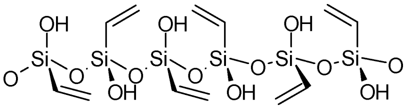
Scheme 9. Thermal Decomposition of 2-Si-ethanesulfonic Acid Groups



of 1-Si-ethanesulfonic acid (**A** structure in Scheme 8) to the total concentration of bonded groups. In the ^{13}C MAS NMR spectrum of SiO_2-R-SO_3H (1), signals at 129 and 136 ppm were detected and assigned to the carbon atoms of residual vinyl groups: $-CH_2{=}\mathit{C}H-Si$ and $-\mathit{C}H_2{=}CH-Si$, respectively. Peaks at 7 and 47 ppm were assigned correspondingly to the $-\mathit{C}H_2-Si$ and $-\mathit{C}H_2-SO_3H$ fragments of 2-Si-ethanesulfonic acid. The only weak signal observed at 23 ppm can be assigned to the $-CH_3$ group in 1-Si-ethanesulfonic acid (but it can also be the $C-CH_2-C$ fragment in 2,4-Si-butanesulfonic acid (**C** structure in Scheme 8). It was a challenge to try TPD-MS to characterize such a complex interface. As can be seen from Figure 7, SiO_2-R-SO_3H decomposes upon heating in vacuum at 448 and 653 K, evolving SO_2 (m/z 64) and C_2H_4 (ions with m/z 28 ($C_2H_4^+$), 27 ($C_2H_3^+$), and 26 ($C_2H_2^+$)). A low-temperature feeble process was assigned to the decomposition of 1-Si-ethanesulfonic acid (**A**), while the higher temperature process was assigned to the decomposition of an acid having the **B** structure (Scheme 8). This assignment is based on the contribution of **A** and **B** isomers to the total loading of immobilized alkylsulfonic acid (see DRIFT data above). The thermal decomposition reaction of the SiO_2-R-SO_3H bonded layer can be presented by Scheme 9. In the SiO_2-R-SO_3H interfacial layer, moiety **C** should have about the same thermal stability as moiety **B** (Scheme 8) since the $-SO_3H$ group is situated in the β-position relative to the Si atom for both mentioned fragments. Comparing the areas of peaks for SO_2 evolution, it can be found that the less stable species **A** comprises 7% of the total SO_2 evolution and the more stable species **B** and **C** 93%. So SiO_2-R-SO_3H can be presented as CMS having mainly 2-Si-ethanesulfonic acid.

In the TPD-MS of SiO_2-R-SO_3H (2) having a "monomeric" structure of the grafted layer, in addition to ethylene and SO_2, ions with m/z 56 (C_4H_8) and 42 (C_3H_6) as well as their fragments were detected (Figure 7). The maximum of propene and butene formation was observed at 640 K and overlaps with the one of SO_2 formation. We believe that these fragments are fingerprints of 2,4-Si-butanesulfonic acid (moiety **C** on Scheme 8) decomposition. Interestingly, for SiO_2-R-SO_3H (1) having a "polymeric" structure of the surface layer (see Table 2), neither C_3H_6 nor C_4H_8 ions were detected among the decomposition products. So 2,4-Si-butanesulfonic acid probably is not formed from $SiO_2-C_2H_3$ with a "polymeric" structure of the grafted layer. This difference between "monomeric" and "polymeric" samples can be explained by the orientation effect. The immobilized groups in "monomeric" interfacial layer had "excited" or "brushed" structure[2,9] for which free-radical reaction with $NaHSO_3$ can give species **C**. Instead, in the "polymeric" layer, the vinyl groups are disordered (Scheme 10). The rigidity of the polysiloxane matrix may prevent them from interacting with each other for the formation of a moiety with structure **C**, Scheme 8.

Scheme 10. Vinyl Groups in the "Polymeric" Grafted Layer



IV. Conclusions

The thermal transformations of organic groups covalently grafted on silica surface usually include reactions between grafted groups and silanols. In this case the decomposition processes have two steps: (1) at 400−700 K immobilized organic groups react with neighboring silanols; (2) only at temperatures above 700 K when migration of silanols becomes possible, the reaction of the grafted layer with remote silanols is prompted. Thermal methods (TGA, DTA, and TPD-MS), especially in combination with traditional spectral methods (IR and MAS NMR), allow the investigation of the interfacial layer fine structure. Special attention should be given to TPD-MS characterization of multifunctional CMSs.

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