Kinetic Analysis of the Thermal Processing of Silica and Organosilica

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ABSTRACT

The incorporation of an organic group into sol-gel derived silica causes significant changes in the structure and properties of these materials. Therefore, the thermal treatment of organosilica materials may require a different approach. In the present paper, kinetic parameters (activation energy, pre-exponential constant and reaction models) have been determined from mass loss data for the dehydration, dehydroxylation and decomposition reactions that take place upon heating silica and organosilica. Parameters were obtained by employing model-free isoconversional methods to data obtained under multiple heating rates, as well as multivariate analysis of the kinetics using a multistep reaction model with distributed activation energy. For silica, it can be concluded that the reaction atmosphere (i.e., inert or thermo-oxidative) has no influence on the reaction rate of the dehydration and dehydroxylation reactions that are responsible for the densification of the material. Under inert atmosphere, full dehydration can be reached without affecting the organic moiety. Achieving complete dehydroxylation of the organosilica is

practically impossible, as decomposition does manifest itself under commonly employed calcination temperatures. This indicates that prudence is required in designing a heat-treatment program for these hybrid materials. To aid in optimizing the thermal treatment, a predictive model was developed, which can be used to forecast the extent of dehydration, dehydroxylation, and decomposition reactions under a multitude of temperature programs.

Keywords: Isoconversional analysis, multivariate analysis of kinetics, hybrid organic-inorganic silica, quantitative kinetic predictions, BTESE

Introduction

Organosilica layers are used in a multitude of applications, including membranes ¹⁻³, low- κ dielectrics ^{4,5}, and optical coatings ^{6,7}. The properties of these layers can be tailored by a thermal treatment, in which temperature and duration can be changed to obtain the desired properties. Densification of pure silica is classically achieved by using high temperatures (> 300 °C) and long treatment times (> 1 hr). However, lower treatment temperatures and shorter treatment times are desired to prevent decomposition of the organic moiety in organosilicas ^{8,9}, to decrease energy use during calcination, or to allow for application of the layer on a supporting substrate with a limited thermal stability ¹⁰⁻¹³. Researchers have investigated several strategies to limit the treatment temperature or duration for hybrid and inorganic systems: a long-term treatment at low temperatures ¹⁴, flash heating at high temperatures ¹⁵⁻¹⁹, or a treatment with acids that renders thermal treatment unnecessary ².

To obtain a material with a targeted microstructure, one is preferably able to predict and steer the thermal processing. Detailed information on the kinetics of the thermally-activated processes that occur during the calcination of organosilica is required to predict the influence of the thermal treatment. This kinetic data is commonly displayed in the form of the kinetic triplet: the activation energy, the pre-exponential constant, and the reaction model. In the case of a hybrid material such as organosilica, a number of reactions can occur during heating, including dehydration, sintering and decomposition. With every of these reactions specific kinetics are associated. The study of these reactions kinetics requires a model capable of treating multistep reaction mechanisms. Such models have been developed for several inorganic materials, e.g. for cement ²⁰, boehmite ²¹, and a hydride silica ²². To study the effects of a thermal treatment on organosilica materials we take a BTESE-derived organosilica as a model system, and compare it

to purely inorganic, TEOS-derived, silica. The thermal dehydration of silica has been studied extensively in the past. Zhuravlev²³ has presented an overview of the different steps during the dehydration process for silica gels, including activation energies and reaction orders. In this study, the work of Zhuravlev is expanded by comparing silica with organosilica, thus demonstrating the influence of an organic moiety on the thermal properties of these materials.

Determination of the kinetic triplet for solid-state reactions can be done in various ways. For an overview of these methods, the reader is referred to the excellent overview on kinetics of solid-state reactions that has been drafted based on the recommendations of the ICTAC Kinetics Committee²⁴. Kinetic models typically consider the reaction rate a function of only two variables, the temperature T and the conversion α :

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (1)$$

where A is the pre-exponential constant (min^{-1}), E_a is the activation energy (J mol^{-1}), R is the gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$), and $f(\alpha)$ (-) is a reaction model as a function of the conversion. Here, we determine the effective activation energy via a model-free isoconversional method^{25–27}, and estimate the corresponding pre-exponential constant via the compensation effect²⁴. The obtained parameters are called ‘effective’ parameters, as they do not necessarily refer to an intrinsic, individual reaction step²⁴. For the sake of readability, we refer to the activation energy without the adjective ‘effective’ from here on. The full reaction model is determined by a multivariate fitting to the experimental data. A complete description of the used models is given in section **Error! Reference source not found.**. The thus obtained fitting parameters are used to comprehend the thermal treatment process of organosilica materials, and can be used in further studies to predict thermal stability of the hybrid and inorganic materials.

Experimental

Materials

TEOS (for synthesis, Merck), BTESE (pur. 97%, ABCR Germany), dried ethanol (max 0.01% H₂O, SeccoSolv[®], Merck), ethanol (absolute for analysis, EMSURE[®], Merck) and nitric acid (1M, Titrisol[®], Merck and $\geq 65\%$ (T), Sigma-Aldrich) were used as received. Water was deionized to 18.2 M Ω cm⁻¹ using a Milli-Q Advantage A10[®] system (Millipore). Oxygen and nitrogen used for TGA-MS were dried with molecular sieve water absorbers. Oxygen was removed from the nitrogen using an oxygen trap (outlet concentration <1 ppb O₂).

Synthesis

Silica and organosilica sols were prepared via the acid-catalyzed hydrolysis and condensation of TEOS and BTESE, respectively. In a glove box under nitrogen, the silicon precursor was mixed with dried ethanol in a conical flask that was subsequently transferred outside the glove box to an ice bath for cooling. A mixture of HNO₃ and water was added drop-wise to the flask in the ice bath, under vigorous stirring. The thus obtained mixture was heated under reflux at 60 °C for 180 min (TEOS) or 90 min (BTESE). After refluxing, the sol was quenched in an ice bath to prevent further reaction. The obtained sols had a molar ratio of 1:3.8:6.4:0.085 (TEOS:ethanol:water:acid) and 1:10.7:6:0.21 (BTESE:ethanol:water:acid).

To obtain powders, the solution was poured into a Petri dish and the ethanol was allowed to evaporate overnight. The obtained flakes were ground to a powder and were placed in a stove at 80 °C for 60 min. The samples were mixed thoroughly with a spatula after 30 min. The powders were stored at room temperature in glass vials until further use.

TGA-MS

Thermogravimetric analysis (TGA) was performed on a STA 449 F3 Jupiter[®] (Netzch), fitted with a TG-only sample holder. Measurements were performed under 70 ml min⁻¹ synthetic air (20% O₂ in N₂) or 70 ml min⁻¹ nitrogen, with heating rates β of 5, 10, 15, and 20 °C min⁻¹, from room temperature to 1000 °C. Temperature calibration was done using melting standards; measurements were run sample-temperature controlled. Blank corrections with an empty cup were carried out at every different heating rate. Sample masses were determined in-situ, exactly 30 min after starting purge gas flow rate. Using a consistent residence time in the purge gas prior to measurement was found to be a crucial parameter to obtain reproducible TGA-graphs.

Gases evolving during the thermogravimetric analysis were transferred to a mass spectrometer (MS, QMS 403 D Aëolos[®], Netzch). TGA and MS start times were synchronized, but no correction was applied for the time offset caused by the transfer line time (estimated < 30 sec, systematic offset). First, a bar graph scan for $m/z = 1-60$ amu was recorded for both silica and organosilica under both nitrogen and air, to determine the evolving m/z -numbers (data not included here). The detected m/z -numbers (2, 12-19, 25, 26, 28-32, 40-46) were selected and recorded more accurately in multiple-ion-detection mode, with a dwell of 0.5 sec per m/z -value and a resolution of 50.

Theoretical calculations

Analysis of TGA data using advanced isoconversional analysis

The mass loss as a function of time and temperature was determined using TGA under multiple different heating rate programs. The mass change was converted to conversion α and normalized between 0 and 1. From the data, activation energies were determined following the integral isoconversional method proposed by Vyazovkin and Dollimore²⁵, using the modified integral for

non-linear temperature programs ²⁷ and variation of the activation energy as a function of conversion ²⁶. The activation energy is obtained by minimizing the function $\Phi(E_\alpha)$:

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (2)$$

where $i = 1..n$ and $j = 1..n$ indicate measurements under different heating programs. In this formula, the integral J is given by:

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_\alpha - \Delta\alpha}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \quad (3)$$

The integral in equation (3) cannot be solved analytically and was therefore approximated numerically; the minimization of equation (2) was done using MATLAB's *fminsearch* algorithm ²⁸.

Overall data fitting using multivariate analysis of the kinetics

A multivariate analysis of the kinetics was used to fit the different heating rate curves obtained by TGA with a multistep parallel reaction model represented by ²⁹:

$$\frac{d\alpha_i}{dt} = A_i \exp^{-E_{\alpha,i}/(RT(t))} f_i(\alpha_i) \quad (4)$$

Where i denotes the i th reaction with weighing factor w_i , where the total conversion is given by:

$$\alpha = \sum_i^n w_i \alpha_i \quad \text{and} \quad \sum_i^n w_i = 1 \quad (5)$$

To obtain physically realistic values for the kinetic triplet, the risk of overfitting needs to be avoided ²⁴. To this end, we took the following approach: the number of reaction steps was determined by evaluating the main steps in TGA and MS data; steps with only a small impact on the mass loss were disregarded for the model fit. Initial values for the multistep mechanism were

taken from the previously determined model-free activation energy, and the corresponding pre-exponential constant as determined via the compensation effect that is manifested in the method of invariant kinetic parameters²⁴. The truncated Sestak-Berggren model ($f(\alpha) = \alpha^m (1-\alpha)^n$) was used to represent the reaction model. MATLAB's build-in *ode23*-solver was used to integrate equation (4)²⁸. Instead of using a single activation energy, the activation energy was modeled as a Weibull-distribution³⁰, in which all the activation energies are associated with independent parallel reactions satisfying equation (5). Minimization of the Residual Sum of Squares (RSS) was performed using MATLAB's *patternsearch* algorithm to detect the global minimum RSS, followed by a run of *fminsearch* to detect the exact position of the minimum²⁸.

Results and discussion

Thermogravimetric analysis and mass spectrometry

Figures 1 and 2 display the mass loss curve and the primary evolved gases during the thermal treatment of silica under nitrogen and air, respectively (an overview of all MS-peaks is given in figures S1 and S2 in the supporting information). The evolution of the mass of silica is similar under inert (nitrogen) and oxidative (air) atmosphere, with the bulk of the mass loss come to pass below 250 °C and a second mass loss step between 250 and 375 °C. Above 375 °C, further mass loss occurs gradually and individual steps cannot be identified.

Analysis of the evolved gases associates the mass loss steps with the release of specific compounds. The primary mass loss is mainly caused by dehydration. Other, minor compounds that are released are NO_x (from HNO₃ catalyst), ethoxy-groups (from reactant and/or solvent), and $m/z = 44$, assigned to either C₂H₄O or CO₂ (from reactant and/or solvent). Under an inert atmosphere, C₂H₄O can be formed by the catalytic conversion of ethanol (or ethoxy-groups) to acetaldehyde and derivatives thereof^{31,32}. Under air, further oxidation to CO₂ is the most probable explanation for the $m/z = 44$ signal. The peak shape of the evolved gases is slightly different under an inert atmosphere than under air, indicating a thermo-oxidative influence under air. However, the impact of this effect is not high enough to cause significant visible differences in the mass loss. At 325 °C, the peak in the mass loss rate is caused by dehydroxylation of (mainly vicinal) silanol groups²³. The removal of hydroxyl-groups continues gradually up to 1000 °C. Because of an increase in isolation of the silanol-groups, the rate keeps decreasing.

Figure 1: Mass loss and first derivative thereof (top) and evolved gases (bottom) as a function of temperature for silica, heated under nitrogen at 20 °C min⁻¹. The assigned m/z signals are: oxygen 16, water 18, acetylene 26, NO_x 30, ethanol 31, CH₂CH(OH) and/or CO₂ 44, and NO₂ 46.

Figure 2: Mass loss and first derivative thereof (top) and evolved gases (bottom) as a function of temperature for silica, heated under air at 20 °C min⁻¹. The assigned m/z signals are: hydrogen 2, water 18, acetylene 26, NO_x 30, ethanol 31, CH₂CH(OH) and/or CO₂ 44, and NO₂ 46.

Figures 3 and 4 display the weight loss curve and the primary evolved gases during the thermal treatment of silica under nitrogen and air, respectively (an overview of all MS-peaks is given in figures S3 and S4 in the supporting information). The differential mass loss curves reveal four dominating mass loss processes. Two of these processes appear similar under both atmospheres: a dehydration step and a sharp decomposition step in which mainly NO_x is released, taking place in the range of 25 – 250 °C. These results agree with the processes occurring for the thermal treatment of silica, although the extend of the weight loss is different, which is caused by the different Si-precursor: HNO_3 :water ratio used in the synthesis of both materials.

Under inert atmosphere, a third mass loss step takes place between 250 and 375 °C. As with silica, this weight loss originates mainly from dehydroxylation of the material. The organic moiety remains intact until 500 °C, where the onset of a release of methane and hydrogen indicate its decomposition. The presence of methane in the evolved gases reveals that the decomposition of the ethyl-bridge takes place through scission of the carbon-carbon bond. The continuous release of hydrogen up to 1000 °C indicates that hydrogen-containing organic material is still present at these temperatures. The carbonous residue that would result from this dehydrogenation is confirmed by the black appearance of the organosilica after the TGA-experiment.

Under an oxidative atmosphere, the gradual decomposition of the organic moiety initiates at 250 °C. Here, gas release takes place in the form of methane, acetaldehyde, and $\text{C}_2\text{H}_4\text{O}/\text{CO}_2$, indicating that the majority of the decomposition takes place via a thermo-oxidative pathway. The different ratios of the evolved gases with respect to temperature show that the decomposition takes place via a complex multistep mechanism. The apparent drop in the methane release at 625

°C can be assigned to the thermo-oxidation of the methane³³. The weight loss rate goes down to zero only at 1000 °C.

Figure 3: Mass loss and first derivative thereof (top) and evolved gases (bottom) as a function of temperature for organosilica, heated under nitrogen at 20 °C min⁻¹. The assigned m/z signals are: hydrogen 2, methane 15, water 18, acetylene 26, NO_x 30, unknown 41, CH₂CH(OH) and/or CO₂ 44, and ethoxy 45.

Figure 4: Mass loss and first derivative thereof (top) and evolved gases (bottom) as a function of temperature for organosilica, heated under air at 20 °C min⁻¹. The assigned m/z signals are: methane 15, water 18, acetylene 26, NO_x 30, CH₂H₄O and/or CO₂ 44, ethoxy 45, NO₂ 46

Determination of activation energies via isoconversional analysis

Figure 5 shows the apparent activation energy as a function of conversion for silica and organosilica, as obtained from the advanced isoconversional method (2), calculated from the data presented in figures S5-S12. Data is given for treatment under nitrogen (open circles) and air (closed squares). The calculated activation energy is an effective average over the individual reactions that occur at a given degree of conversion. Based on the TGA-MS results (section 0), the major reaction steps can be assigned as shown in

Table 1.

Figure 5: Apparent activation energy determined by the isoconversional analysis of TGA-data for the thermal treatment of silica (a) and organosilica (b) under nitrogen (●) and air (□). Data for organosilica under air is only shown for $\alpha = 0 - 0.25$ and $\alpha = 0.7 - 1$, because of non-physical values for the data in this region (see text). The full version of the graph can be found in figure S13.

Table 1: Assignment of occurring processes to the mass loss of silica, both under inert atmosphere and air

Conversion	Process	E_a (kJ mol ⁻¹)
0-0.6	Dehydration	76±3
0.6-0.75	Dehydration	76 - 300
	HNO ₃ catalyst decomposition	
	Solvent/ethoxy-group	
0.75-0.90	Dehydroxylation	150 – 300
0.90-1	Dehydroxylation (thermodynamically limited)	Accurate determination not possible

The TGA-MS reveals two major steps in the mass loss. The first is a dehydration step, for which the activation energy for both atmospheres lies within the margins of error. A constant value of the activation energy typically implies that a single reaction dominates the mass loss process²⁴. The activation energy reported for this step by Zhuravlev, 25 – 42 kJ mol⁻¹²³, is a factor 2-3 lower than the value calculated here. This difference can be caused by the different microstructure (this study: microporous; Zhuravlev's study: mesoporous) if the activation energy is associated with the diffusion process of the water out of the silica network. It has been demonstrated that decreasing pore sizes lead to higher activation energies for diffusion of several gases³⁴, and water in particular³⁵. Alternatively, this difference may be a result of the use of a single heating rate mass loss curve by Zhuravlev, a method that was later judged to be unreliable for determining activation energies²⁴. The first mass loss step is shouldered by the decomposition of the ethoxy-groups and the HNO₃ catalyst. In this part, the activation energy is an effective average over the dehydration and decomposition reactions.

The second step is associated with the dehydroxylation of the material. As the amount of vicinal silanol groups decreases, more silanol groups become isolated. However, two silanol

groups are required for the condensation reaction with the release of water. Because of their isolation, the convergence of silanol groups becomes less frequent, and the activation energy for dehydroxylation rises ²³. With increasing conversion, the mass loss rate decreases, and the relative error in the conversion decreases, leading to scatter in the activation energy data. Above 90% conversion, the low mass loss rate causes the different heating rate curves to lie close together; because the error in the mass loss becomes similar to the magnitude of the shift in the curves, it is impossible to determine the activation energy in this heating rate range.

Describing the kinetics of dehydration, dehydroxylation and decomposition is more complex for organosilica, since the decompositions of the organic bridging group overlaps (part of) the other processes. Table 2 gives an overview of the specific processes responsible for the mass loss as a function of conversion (see section 0 for the assignments).

Table 2: Assignment of specific processes to the mass loss conversion of organosilica, both under inert atmosphere and air

Conversion	Under N ₂	E_a (kJ mol ⁻¹)	Under air	E_a (kJ mol ⁻¹)
0-0.25	Dehydration	91.7±3.9	Dehydration	130-180
0.25-0.45	Dehydration	90 - 180	Dehydration	*
	Catalyst decomposition		Catalyst decomposition	
	Solvent/ethoxy-groups		Solvent/ethoxy-groups	
0.45-0.70	Dehydroxylation	160 - 190	Many reactions, mainly decomposition or organic moiety	*
0.75-0.95	Decomposition organic moiety	190 - 300	Many reactions, mainly decomposition or organic moiety	*

* Accurate determination of the activation energy was not possible for this step

The TGA-MS under N₂ reveals four major mass loss steps. The first two steps, responsible for the 40% conversion, are a dehydration step ($\alpha = 0$ to 0.25), and a decomposition step of the solvents/ethoxy-groups and the HNO₃ combined with further dehydration ($\alpha = 0.25$ to 0.40). The slightly higher activation energy for the dehydration of the organosilica, as compared to silica, may indicate a difference in the physisorption energy for the two materials, which can be a result from the difference in the pore morphology or and surface chemistry of the materials.

At $\alpha = 0.40$, the activation energy shows an apparent drop. This drop is an artifact of the analysis and is physically not realistic: because the mass loss curves are positioned close together, small errors in the mass cause the curves to crossover, which manifests itself in lower or even negative values for the activation energy. The third step is assigned to the dehydroxylation of the organosilica. Although a small increase in the activation energy is observed, this increase is less strong than that of silica. We hypothesize that the organic linking group in the material provides more dynamics for the silanol group, and stabilizes the partial positive charge on the silicon atom

by electron donation, thus effectively decreasing the energy barrier for dehydroxylation. In the fourth step ($\alpha = 0.75$ to 0.95), decomposition of the organic groups take place.

Under air, the thermal treatment of the organosilica forms a complex mixtures of a multitude of decomposition reactions. The only step that can be identified is the dehydration reaction ($\alpha = 0$ to 0.25). At α -values higher than 0.25 , the calculated values for the activation energies are strongly scattered (between -200 and 800 kJ mol^{-1}) because of a crossover of the mass loss curves (see figure S12). Surprisingly, this crossover is caused by a significant acceleration in the mass loss at higher heating rates. This accelerated mass loss has been observed consistently in triplicate when measurements were repeated (results not shown here). For conversion values higher than 0.70 , the values of the activation energy are physically realistic. However, the unexpected dependence of the mass loss rate on the heating rate indicates that interpretation should be performed with caution. We have therefore limited the determination of kinetic parameters for organosilica to those obtained under inert atmospheres.

Multivariate analysis of the kinetics

Figure 6 shows the results of the multivariate analysis fit to the data acquired for the thermal treatment of silica under nitrogen. Equation (4) was used for the fitting, with the constraints given in equation (5). The mass ratios of the different steps were determined from the vertical asymptote in the model-free activation energy data (in this case, $w_1 = 0.75$ and $w_2 = 0.15$). Both reaction steps were modeled with a Weibull-distributed activation energy for independent parallel reactions. Conversion values larger than 0.9 were omitted, since the magnitude of the shift in the curves was equal to the magnitude of the error. The fit parameters are given in

Table **3**, and the resulting fit is given in Figure 6.

Table 3: Kinetic parameters for the thermal treatment of silica under nitrogen, fitted with a Weibull-distributed activation energy

Conversion	Step 1 ($w = 0.75$) Nitrogen	Step 2 ($w = 0.15$) Nitrogen	Step 1 ($w = 0.75$) Air	Step 2 ($w = 0.15$) Air
A (min^{-1})	$2.65 \cdot 10^{10}$	$2.56 \cdot 10^{16}$	$3.03 \cdot 10^{10}$	$2.47 \cdot 10^{16}$
E_a threshold (kJ mol^{-1})	70.6	164.1	69.2	153.4
β (-)	1.52	1.39	1.98	2.08
η (kJ mol^{-1})	11.4	30.1	13.9	37.3
E_a average (kJ mol^{-1})	81.0	191.5	81.5	186.4
m (-)*	0	0	0	0
n (-)*	1	1	1	1

*Variable not fitted, since it is convoluted with E_a . For nitrogen: $\text{RSS} = 0.0081$, $n = 9604$, $p = 8$, variance = $8.4 \cdot 10^{-7}$. For air: $\text{RSS} = 4.6 \cdot 10^{-7}$, $n = 9604$, $p = 8$, variance = $4.6 \cdot 10^{-7}$.

An identical approach was chosen for the data for BTESE under nitrogen. The mass ratios of the different steps were determined from the vertical asymptote in the model-free activation energy data (in this case, $w_1 = 0.42$ and $w_2 = 0.37$, and $w_3 = 0.15$). All reaction steps were modeled with a Weibull-distributed activation energy for independent parallel reactions. Conversion values larger than 0.95 were omitted, since the magnitude of the shift in the curves was equal to the magnitude of the error. The fit parameters are given in

Table 4.

Table 4: Kinetic parameters for the thermal treatment of BTESE under nitrogen, fitted with a Weibull-distributed activation energy

Conversion	Step 1 ($w = 0.43$)	Step 2 ($w = 0.37$)	Step 2 ($w = 0.15$)
A (min^{-1})	$3.63 \cdot 10^{10}$	$2.75 \cdot 10^{16}$	$1 \cdot 10^{18}$
E_a threshold (kJ mol^{-1})	68.6	156.7	302.7
β (-)	2.52	1.16	0.77
η (kJ mol^{-1})	14.7	48.3	27.6
E_a average (kJ mol^{-1})	81.7	202.6	335.1
m (-)*	0	0	0
n (-)*	1	1	1

*Variable not fitted, since it is convoluted with E_a . RSS = 0.0129, $n = 7206$, $p = 12$, variance = $1.79 \cdot 10^{-6}$

For silica, the results of the model fit show good agreement with the data obtained using the model-free isoconversional analysis. The fit matches the data closely, and only seems to deviate slightly for the first and final parts of the dehydration reaction. For the organosilica, the results deviate from those obtained using the model-free methods; especially in the case of the activation energy of the dehydration reaction which is 10 kJ mol^{-1} lower when determined via the multivariate analysis of the kinetics. Here, this may be caused by a correlation of the activation energy with n , as a pseudo- n -th order reaction is mathematically identical to a gamma distribution or a Weibull distribution (with shape parameter 1) in the activation energy³⁰.

Figure 6: Multivariate fit for the thermal treatment of silica under N_2 . Symbols depict the experimental data, solid lines represent the fit, and dashed lines show the fit residuals.

Model simulations

The obtained data can be predicted to determine the conversion of the reaction steps under a chosen heating program. It should be noted that predictions at temperatures, times, and/or heating rates outside of the measurement range have an inherent inaccuracy because of the propagation of errors in the kinetic predictions. The model returns good results within the original measurement range (β between 5 and 20 $^{\circ}C\ min^{-1}$). To further illustrate the model accuracy, data was simulated

for the thermal treatment of organosilica under N₂ under extrapolated conditions: a linear heating rate of 3 °C min⁻¹ to 500 °C, followed by a two hour dwell. Figure 7 shows that the experimental data closely follows the model simulation. . Further, the model allows for deconvolution of the data for dehydration, dehydroxylation, and decomposition processes, creating the possibility for fine-tuning of the thermal treatment program, e.g. in order to avoid decomposition of the organic moiety.

Figure 7: Simulated data (solid line) and measured data ($\circ$) for the thermal treatment of organosilica under N_2 at a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$ including a two hour dwell at $500\text{ }^{\circ}\text{C}$. The different steps are indicated by the colored area under the graph: dehydration (teal), dehydroxylation (blue), and decomposition (red).

To give guidelines for the thermal processing, Table 5 lists the temperature ranges in which the three identified processes (dehydration, dehydroxylation, and decomposition) occur under three relevant temperature programs: $1\text{ }^{\circ}\text{C min}^{-1}$ and $10\text{ }^{\circ}\text{C min}^{-1}$ as the bound for commonly used heating ranges, and $100\text{ }^{\circ}\text{C min}^{-1}$ as an identifier for flash-heating process.

Table 5: Temperature ranges in which the studied processes take place, for silica and organosilica under nitrogen for three different linear heating rates

Temperature range for designated process (°C) for heating rates of:				
	1.1	1 °C min ⁻¹	10 °C min ⁻¹	100 °C min ⁻¹ *
* <hr/>				
<i>Silica</i>				
Dehydration	33-187	52-228	79-276	
Dehydroxylation	204-482	230-525	258-573	
Decomposition	-	-	-	
<hr/>				
<i>Organosilica</i>				
Dehydration	34-159	53-197	80-242	
Dehydroxylation	185-714	209-770	237-832	
Decomposition	500-1071	537-1139	578-1216	

Temperature ranges are given as $T_{\text{start}} - T_{\text{end}}$, where T_{start} is defined as $\alpha = 0.01$, T_{end} is defined as $\alpha = 0.99$. * These heating rates are an extrapolation of the measured data.

Conclusions

The first step in the thermal treatment of silica-based materials is the removal of physisorbed water from the material. By isoconversional analysis, an effective activation energy of 76 ± 3 kJ mol⁻¹ was calculated for the dehydration of silica, irrespective of the atmosphere in which the material is treated, and an effective activation energy of 91.7 ± 3.9 kJ mol⁻¹ was calculated for the dehydration of the organosilica under inert atmosphere; under air atmosphere, it was impossible to determine a single activation energy for the dehydration of the organosilica. The activation energy for dehydration of the organosilica is roughly 20% higher than that for plain silica; we hypothesize that this is caused by a difference in the binding of the water to the material as a result of the organic bridging group. In both cases, the activation energy is significantly higher

than the activation energy for evaporating water, $40 - 43 \text{ kJ mol}^{-1}$ ³⁶, suggesting that the water is strongly bound.

The second process that is manifested through the loss of water is the dehydroxylation of the material. For silica, the dehydroxylation reaction has an effective activation energy of $150 - 300 \text{ kJ mol}^{-1}$, and is strongly dependent on the degree of conversion. The strong increase in activation energy is attributed to the increasing spatial separation of the silanol groups, which makes dehydroxylation more difficult. For organosilica, this activation energy is fairly constant at $160 - 190 \text{ kJ mol}^{-1}$; it is hypothesized that this is a result of the enhanced mobility of the organosilica framework that is provided by the organic bridging group.

The third process that is encountered is the decomposition of the organic moiety for organosilica. Under nitrogen, the effective activation energy of this process could be determined to range from $190 - 300 \text{ kJ mol}^{-1}$. Under air, dehydroxylation and decomposition reactions take place simultaneously, rendering it impossible to accurately determine the kinetics of this reaction step.

For organosilica the kinetics of the dehydration, the dehydroxylation, and the decomposition of the organic moiety could be modeled via a multivariate analysis. The developed model allows for a prediction of the conversion of the different reactions as a function of temperature and time. Model simulations for extrapolated heating rates are in excellent agreement with experimentally obtained data. Model simulations for linear heating rates show that full dehydroxylation is always accompanied by a certain extent of decomposition.

Mass loss may not be the sole predictor for the microstructure of a material, as reactions without or with minor mass loss can be decisive in the formation process. Nonetheless, important steps such as dehydration, dehydroxylation, and decomposition of organic moieties can be

tracked through their mass loss, especially when the evolved gases are analyzed. The determination of reaction kinetics on the basis of TGA/MS-data can form an important addition to the trial-and-error optimization of thermal treatment schemes, and can be used to predict the thermal stability of the synthesized materials.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work is supported by the Helmholtz Alliance MEM-BRAIN, funded by the Initiative and Networking Fund of the Helmholtz Association.

Acknowledgements

The authors acknowledge the funding of this work by the Helmholtz Alliance MEM-BRAIN. The authors would like to acknowledge the help of Cindy Huiskes with setting up the TGA-measurements.

Supporting Information

Supporting Information Available: The supporting information contains all data for the mass spectrometry and thermogravimetric analysis that were used for this article. This material is

available free of charge via the Internet at <http://pubs.acs.org>.

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Table of Contents graphic

Table of Contents graphics: The materials silica and organosilica have been studied by thermogravimetric analysis under varying heating rates. Analysis with isoconversional analysis and a multivariate analysis of the kinetics result in the values for the kinetic triplet, which allow for prediction of the thermal processing of these materials.