Calorimetric Study of the Effect of Water Quantity on Tetramethoxysilane Hydrolysis under Ultrasound Stimulation

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The ultrasound stimulated and oxalic acid-catalyzed hydrolysis of tetramethoxysilane (TMOS) was studied by means of a heat flux calorimetric method as a function of the initial water/TMOS molar ratio (r) ranging from 2 to 10. The method is based on the time recording of the hydrolysis exothermic heat peak, which takes place in acidulated heterogeneous water−TMOS mixtures under ultrasonic stimulation, accounting for the instantaneous hydrolysis rate. The hydrolysis rate increases from zero up to a maximum value during the heterogeneous step of the process and then diminishes naturally according to the reactant consumption. The total hydrolyzed quantity was found to be slightly increasing with r. The immiscibility gap of the TMOS−water system in the presence of the hydrolysis products has been inferred from the evaluation of the reacted quantity during the heterogeneous step of the reaction and it has been represented in a ternary diagram in the studied r-range.

Introduction

A large variety of glass and glass ceramics have been obtained by a sol−gel process from the hydrolysis of silicon alcoxide, mainly tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS).[1] Since the alkoxide-water system exhibits frequently an immiscibility gap, a cosolvent such as alcohol is used as homogenizing medium for the hydrolysis process. Ultrasound is an alternative method to promote hydrolysis of alkoxides without using an alcoholic cosolvent for homogenization of the mixtures.[2] Under the sono-hydrolysis process, the hydrolysis rate is practically zero at the beginning of the sonication. Ultrasound acts as an effective starter for the reaction by fast mixing the system, promoting cavitation and increasing the effective contacting area between alkoxide and water. The product of hydrolysis (alcohol and silanol) helps the mutual dissolution, causing further enhancement of the reaction rate. The reaction rate increases up to a maximum value, attained at a time t_p, during the heterogeneous step of the reaction, and then decreases naturally as a function of the reactant consumption. The hydrolysis rate has quantitatively been related to the thermal peak due to the heat release of the hydrolysis reaction under ultrasound stimulation and has been measured by a calorimetric method.[3−6] The results have been interpreted on the basis of dissolution and reaction modeling, and the method has been applied to study the hydrolysis of TEOS[6−8] and of TMOS.[9]

As the final product is strongly dependent on the initial conditions of preparation, we probe, in the present work, the effects of the initial water quantity on the sono-hydrolysis of TMOS catalyzed by oxalic acid by means of the mentioned calorimetric method, ranging the initial water/TMOS molar ratio (r) from 2 to 10. The results allowed us to infer part of the immiscibility gap from the evaluation of reacted quantity during the heterogeneous step of the reaction. A relatively weak acid has been used as a catalyst in order to diminish the rate of the

frequently rapid TMOS hydrolysis to allow the process to be followed by the present experimental method. Besides that, oxalic acid produces a narrower and larger pore size distribution in the resulting gel, which favors a posterior drying processes in obtaining of monoliths.[1]

Experimental Section

Materials and Sono-Hydrolysis. Tetramethoxysilane (TMOS), distilled and deionized water, and oxalic acid as a catalyst were used to prepare acidulated TMOS−water mixtures of constant volume (31 mL) with 0.116 mol/L oxalic acid and water/TMOS molar ratio (r) ranging from 2 to 10. The samples were submitted to a constant power (60 W) of ultrasonic radiation using a 20 kHz, 600 W apparatus, with a 13-mm-diameter titanium transducer driven by an electrostrictive device. As described elsewhere,[3] a stainless steel reaction cell is held at a thermostatic temperature by means of high flux water circulation from an external bath. When the ultrasound is set on, under the condition of no catalyst, the temperature of the reactant mixture reaches rapidly a steady-state value (T_R), which was found to be about 3 °C above the temperature (T_e) of the circulating bath. With the addition of the catalyst (oxalic acid), under continuous sonication, the hydrolysis reaction starts rapidly increasing the temperature (T) of the mixture, giving rise to a thermal peak $\Delta T_t = T - T_R$, as a function of the sonication time (t), which accounts for the time hydrolysis rate.[5] Temperature versus sonication time patterns, carried out at $T_e = 25$ °C, were obtained, by means of a chromel/constantan thermocouple coupled to an A/D converter and microprocessor, as a function of the initial water/TMOS molar ratio (r) ranging from 2 to 10.

Interpretation of Calorimetric Data. The power of the heat delivered to the system (P) by the ultrasonic tip probe under a heat flow steady state, as that verified when no catalyst is present and the temperature reaches the stationary value T_R, can be cast as

$$P = k\Delta T_R \tag{1}$$

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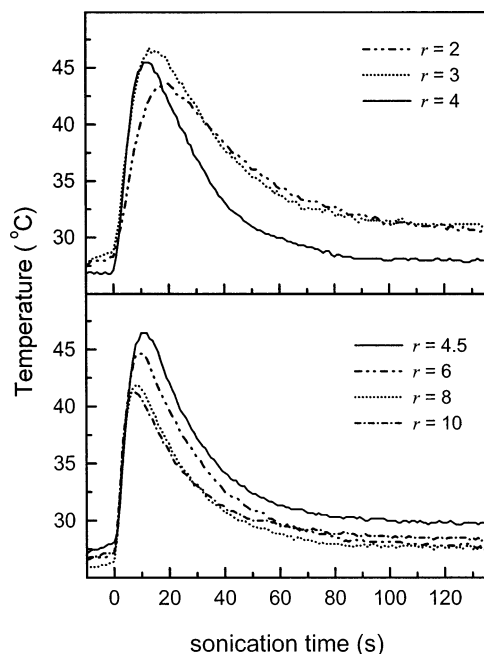
Figure 1. Temperature versus sonication time patterns as obtained for oxalic acid acidulated TMOS−water mixtures of constant volume with different water/TMOS molar ratio (*r*) under continuous ultrasound stimulation. The thermal peak in each case accounts for the hydrolysis reaction rate.

Figure 2. (a) The thermal peak area normalized by the initial TMOS quantity in the TMOS−water mixtures of constant volume as a function of water/TMOS molar ratio (*r*). (b) The baseline shifting due to the difference between the product steady-state temperature after hydrolysis and the reactant steady-state temperature before hydrolysis. The dashed line was drawn to guide the eyes.

where $\Delta T_R = T_R - T_e$ and k is a parameter which is a function of the geometry and the thermal process of heat transfer through the medium.

When the catalyst is added, an additional liberation of heat, due to the hydrolysis reaction, increases the instantaneous temperature of the mixture by the additional amount $\Delta T_t = T - T_R$ with respect to T_R. If $d[C]/dt$ is the hydrolysis rate, where $[C]$ is the concentration of the product of the hydrolysis, and ΔH the reaction heat, the rate of the additional heat release is $\Delta H(d[C]/dt)$. Neglecting the effects of thermal retention due to the thermal capacity of the system when compared to the high term associated to the heat flow, and assuming an instantaneous steady state heat flow as eq 1 with this additional power of heat release, we can write

$$P + \Delta H \frac{d[C]}{dt} = k(\Delta T_R + \Delta T_t) \qquad (2)$$
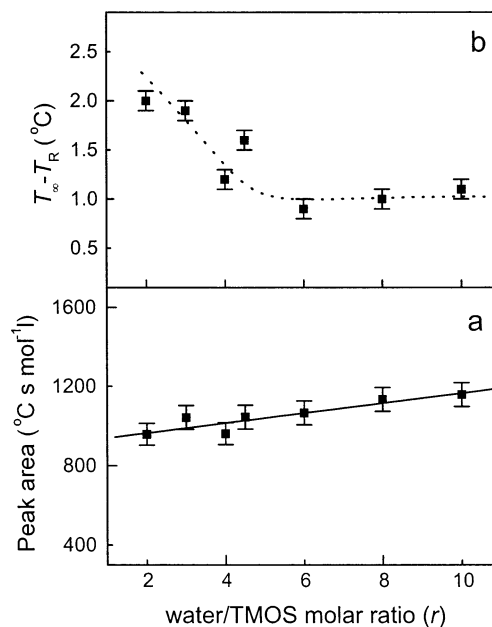
and by eq 1 we can cast

$$\frac{d[C]}{dt} \propto \Delta T_t \qquad (3)$$

Equation 3 allows the determination of the instantaneous reaction rate, in relative units, from the experimental ΔT_t vs t patterns. Integrating eq 3 from the initial condition $t = 0$ when $[C] = 0$ up to $t = \infty$ when $[C] = A_o$ (the total TMOS molar concentration to react) and using this result as a normalization parameter, we obtain $[C]$ in mol L^{-1} units as

$$[C] = A_o \int_0^t \Delta T_t \, dt \Big/ \int_0^\infty \Delta T_t \, dt \qquad (4)$$

Results

Figure 1 shows the experimental TMOS−water mixture temperature (*T*) versus sonication time (*t*) patterns as obtained

at $T_e = 25\ °C$ by varying the water/TMOS molar ratio (*r*) from 2 to 10. The initial zero time ($t = 0$) was set at the instant when the oxalic acid was added to the mixture under ultrasonic stimulation. The exothermic peak ΔT_t inferred from the temperature increase shown in Figure 1 accounts for the TMOS hydrolysis rate as established in eq 3. The volume of the samples was found practically unchanged after the rapid hydrolysis peak.

The integration of the thermal peak should yield the total hydrolyzed quantity according to eq 4. Figure 2a shows the peak area normalized with respect to the initial quantity of TMOS as a function of the water/TMOS molar ratio. Apparently the total hydrolyzed quantity slightly increases with the initial water quantity. We have noted that the steady-state temperature (T_∞) beyond the thermal peak was slightly different from the steady-state temperature T_R, the difference depending on *r*. Figure 2b shows $T_\infty - T_R$ as a function of *r*. The more notable differences were found for $r < \sim4$. We attributed this behavior to small differences in the reaction products. Small modifications in the properties of the medium, as viscosity and thermal properties, should influence the heat flow through the medium and modify the dynamic characteristics of the calorimeter, causing a slight shifting of the steady-state temperature beyond the thermal peak. So, we conclude that some polycondensation reaction should be occurring mainly for small *r* values. This supposition is in agreement with NMR studies[10] carried out in the analogous TEOS system. Furthermore, we have noted that an abrupt increase in the polycondensation rate, carried out by an instantaneous addition of NH$_4$(OH), does not cause a substantial contribution to the hydrolysis thermal peak.[3] Thus the thermal peak is a contribution almost exclusively of the hydrolysis reaction. Therefore, polycondensation should be taking place mainly for $r < 4$ in order to release water for further hydrolysis so the total hydrolyzed quantity could be found almost independent of *r*, as suggested by the normalized peak area in Figure 2a. We think that possible complexation reactions due to the presence of the weak acid are not important under this relatively rapid hydrolysis process stimulated by ultrasound.

Effect of Water Quantity on TMOS Hydrolysis

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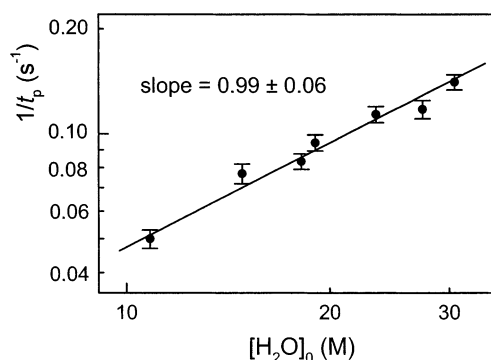
Figure 3. Inverse of the time for the maximum heat release of hydrolysis as a function of the initial molar water concentration. The straight line was obtained by a least-squares linear fitting.

Figure 3 shows the values of the inverse of the peak time (t_p^{-1}) as a function of initial water molar concentration $[H_2O]_0$, on a log–log scale. We have found that t_p^{-1} follows approximately a relationship given by $t_p^{-1} \propto [H_2O]_0$ in the studied r range, since the slope of the straight line of the linear fitting in Figure 3 was found essentially equal to 1. The inverse of the peak time is associated to a certain media for the initial hydrolysis rate during the heterogeneous step of the reaction.

Discussion

The hydrolysis rate equation for the reaction between TMOS (A) and water (B) yielding $Si(OH)_4$ (C) and methanol can be written as

$$\frac{d[C]}{dt} = k_H[A][B] \tag{5}$$

where [C] is the molar concentration of $Si(OH)_4$, [A] and [B] are the molar concentrations of TMOS and water, which are really in contact one with the other since the system is immiscible, and k_H is the hydrolysis rate constant, assumed as being second order in [A] and [B]. We have considered the formation of fully hydrolyzed silicon species $Si(OH)_4$ instead of the partially hydrolyzed ones $Si(OR)_{4-x}(OH)_x$ since we cannot distingue with our calorimetric method a fully hydrolyzed species from four monohydrolyzed species. Then, the measured heat release represents an overall medium value resulting from the hydrolysis heat associated with the four methoxy groups. Under the heterogeneous step of the reaction, the initial condition is such that the hydrolysis rate is essentially zero because the product [A][B] = 0, since A and B are immiscible. Ultrasound starts the hydrolysis by fast mixing the reactant mixture, increasing the contact between TMOS and water. The first appearance of the products, methanol and $Si(OH)_4$, enhances the homogenization of the system, increasing the hydrolysis rate, since [A][B] is increased with the homogenization. The process evolves until the hydrolysis rate eventually reaches a maximum value, at a time t_p, from which it drops naturally according to the reactant consumption, following a fairly homogeneous step for the reaction.

An average value for the hydrolysis rate, $\langle d[C]/dt \rangle_{t_P}$, during the heterogeneous step of the reaction could be obtained by integration of eq 5 from $t = 0$ to t_P. So,

$$\left\langle \frac{d[C]}{dt} \right\rangle_{t_P} = k_H \langle [A][B] \rangle_{t_P} \tag{6}$$

where $\langle [A][B] \rangle_{t_P}$ represents the medium value of the product [A][B] in the heterogeneous step of the reaction. A reasonable
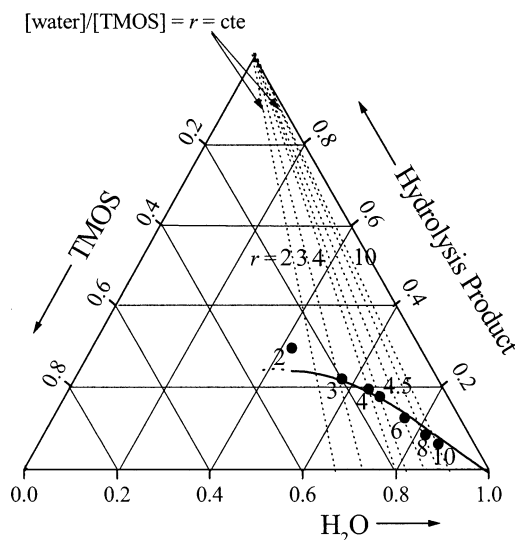
Figure 4. Ternary diagram representing the molar fraction of TMOS, water, and hydrolysis product (methanol and $Si(OH)_4$). The points were plotted by evaluation of the compositions in which the system supposedly crosses the immiscibility gap for each r value. The dashed lines represent the most probable reaction pathways in each case, each one defined by the corresponding relation [water]/TMOS = constant = r. The solid line represents an immiscibility gap line that was sketched throughout the points and the water corner of the diagram.

assumption for the quantity $\langle [A][B] \rangle_{t_P}$ should be a function of the solubility of the system whose amplitude should be proportional to the initial quantities of both TMOS (A_0) and water ($[H_2O]_0$). Then,

$$\left\langle \frac{d[C]}{dt} \right\rangle_{t_P} \propto A_0 [H_2O]_0 \tag{7}$$

On the other hand, the average value of d[C]/dt in the time interval from $t = 0$ to t_p, i.e., $\langle d[C]/dt \rangle_{t_P}$, is obtained from eq 3 as

$$\left\langle \frac{d[C]}{dt} \right\rangle_{t_P} \propto \frac{\int_0^{t_P} \Delta T_t \, dt}{t_P} \tag{8}$$

Since $\int_0^{t_P} \Delta T_t \, dt$ is proportional to A_0, eq 8 can be cast as

$$\left\langle \frac{d[C]}{dt} \right\rangle_{t_P} \propto \frac{A_0}{t_P} \tag{9}$$

Comparing with eq 7 we conclude that

$$\frac{1}{t_P} \propto [H_2O]_0 \tag{10}$$

which is in accordance with the $t_p^{-1} \propto [H_2O]_0$ behavior found in Figure 3.

An alternative way to analyze the heterogeneous step of reaction under ultrasound stimulation can be obtained from the assumption that at the time t_p the system is crossing the immediacies of the immiscibility gap line. Thus, eq 4 applied to $t = t_p$ would yield the molar concentration of the product at the moment in which the system is crossing the immiscibility gap. Using the initial concentrations A_0 and $[H_2O]_0$ and the stoichiometry of the hydrolysis reaction, the concentrations of methanol and nonreacted TMOS and water at time t_p can be evaluated. The evaluation was performed, and the results are represented in a ternary diagram showed in Figure 4 as a

function of the initial water quantity. The points plotted in Figures 4 represent the composition of the system in terms of the molar fraction of TMOS, H_2O, and product of hydrolysis (CH_3OH and $Si(OH)_4$) at the instant $t = t_p$ when the system supposedly is crossing the immiscibility gap line. We included methanol and $Si(OH)_4$ as product to allow a ternary representation. We have bear in mind that product represents 4 mol of methanol and 1 mol of $Si(OH)_4$, so the molar fraction of the product in the diagram is composed by 80% methanol and 20% $Si(OH)_4$. The most probable immiscibility gap line was drawn in Figure 4 in the studied r range. Although we could not find, at first sight, a TMOS−water−methanol phase diagram in the literature for direct comparison, the result seems reasonable if on the basis of the expectation of finding a minor immiscibility gap in the TMOS−water−methanol system when compared to the analogous TEOS−water−ethanol system.[11] The points for small r values are less concordant with the sketched immiscibility gap line due to the greater contribution of polycondensation found in these systems.

Conclusions

The simple calorimetric method employed in this work allowed us to probe the ultrasound and oxalic acid catalyzed hydrolysis of TMOS as a function of the initial quantity of water. The hydrolysis rate is associated to the time hydrolysis peak. The hydrolysis rate increases from zero up to a maximum value during the heterogeneous step of the process and then diminishes naturally according to the reactant consumption. The total hydrolyzed quantity was found to slightly increase with the initial quantity of water. Some polycondensation should be occurring parallel with hydrolysis, mainly for small water/TMOS molar ratio values. The average value of the initial hydrolysis rate, as evaluated during the heterogeneous step of the reaction, is in accordance with a second order hydrolysis rate constant for TMOS and water. The immiscibility gap of the TMOS−water system in the presence of the hydrolysis product in the studied water/TMOS molar ratio range was inferred from the evaluation of the reacted quantity up to the end of the heterogeneous step of the reaction, and it has been represented in a ternary diagram.

References and Notes

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