Determination of hydrolysis and condensation in sol-gel reactions

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Conclusion

For the production of sol-gel-based materials knowledge about the degree of hydrolysis and condensation is essential to create products with designed properties. With the combination of ATR-IR, ^{1}H-NMR, and Karl Fischer titration it is possible to online measure the progress of hydrolysis and condensation during the reaction. Correlation of results show that ^{1}H-NMR measurements provide a method for fast progress measurement in sol-gel reactions.

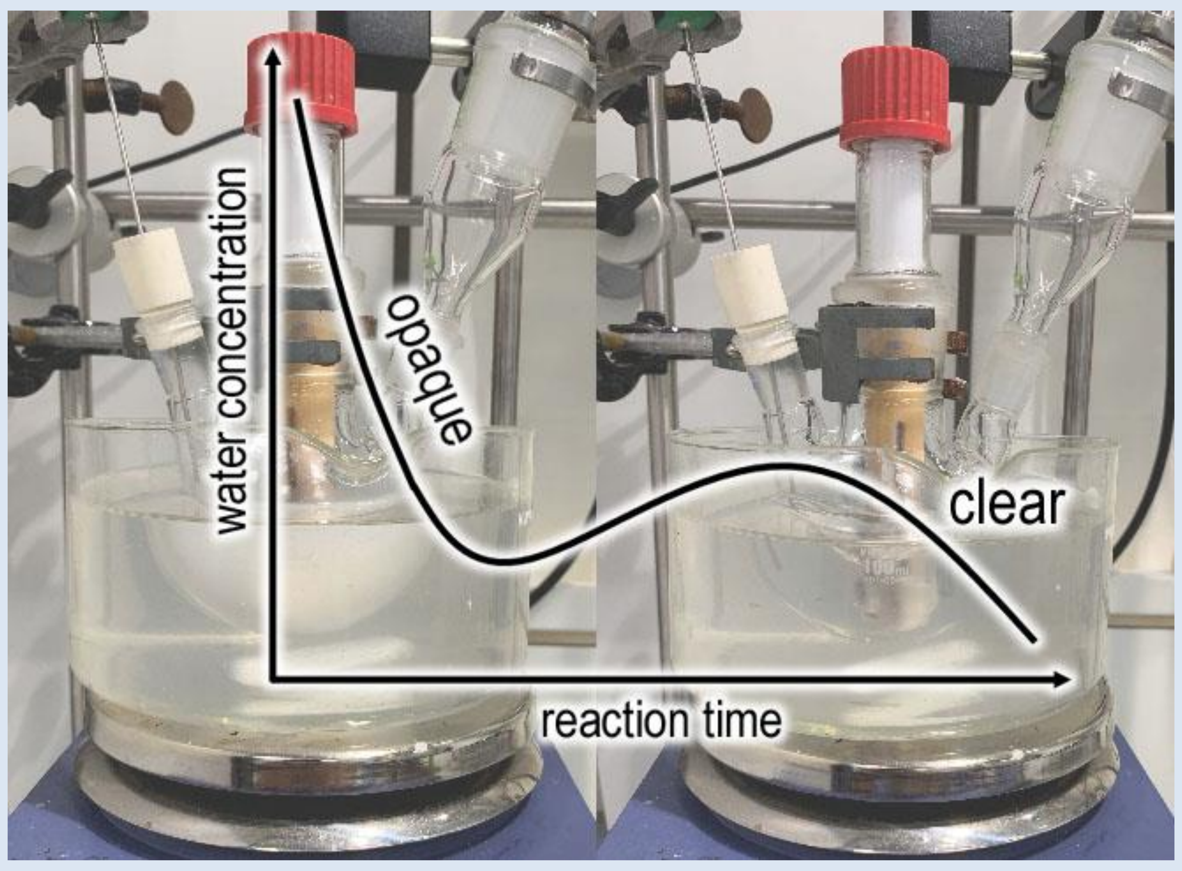

Figure 1: Schematic progress of hydrolysis and condensation for the sol-gel reaction. Opaque reaction solution turns clear after sufficient hydrolysis followed by controlled condensation.

Introduction

Coatings for specialty applications require flexibility, high temperature-, and abrasion resistance. One approach for the production of such coatings is the sol-gel process based on hydrolysis and condensation, shown in Figure 2. These two steps are not entirely separable from each other, however with tailored conditions (temperature, pH-value, amount of water, and catalyst) it is possible to push the reaction towards hydrolysis or condensation. Herein, progress measurements of hydrolysis and condensation with ATR-IR, ^{1}H-NMR, and Karl Fischer titration are shown.

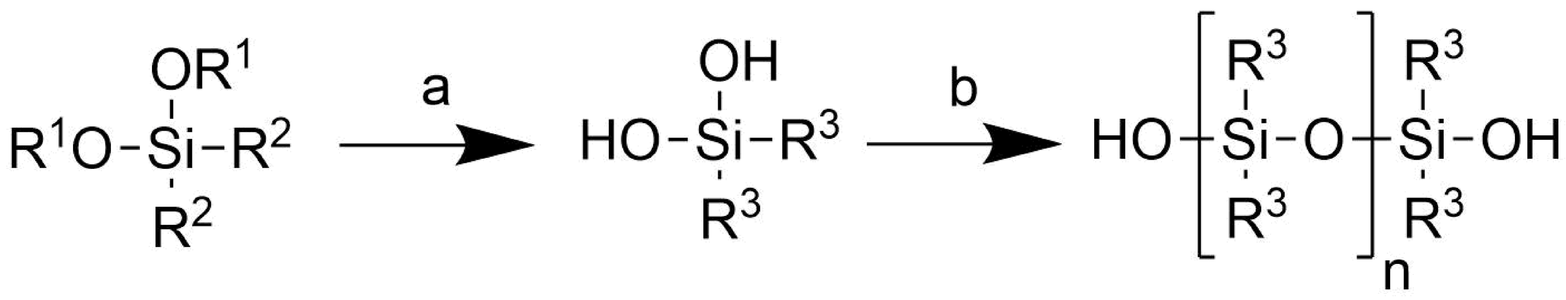

Figure 2: Hydrolysis (a) and condensation (b) of silanes during sol-gel reactions. R^1: Et, Me; R^2: OEt, OMe, Ph, Me; R^3: OH, Ph, Me.

Results and Discussion

Hydrolysis can be favored with a reaction temperature of 60 °C, stoichiometric amount of water, and succinic acid as catalyst. During hydrolysis water is consumed and the solution turns from opaque to clear (Figure 1). Thereby the water concentration decreases to a constant level of 30 – 40 % . In the next step the solution is heated to 150 °C to evaporate water and alcohols. In this step condensation increases which again releases water.

Figure 3 shows ATR-IR spectra of the silane mixture (black), the reaction solution after turning clear (blue) and the final product (red). In the highlighted image section at about 1100 cm^{-1} a decreasing ethoxy signal (representing educts) is observed and attributed to hydrolysis. In the region from 3000 – 3600 cm^{-1} the concentration of all OH-groups (water as well as silanols and alcohols) can be estimated.

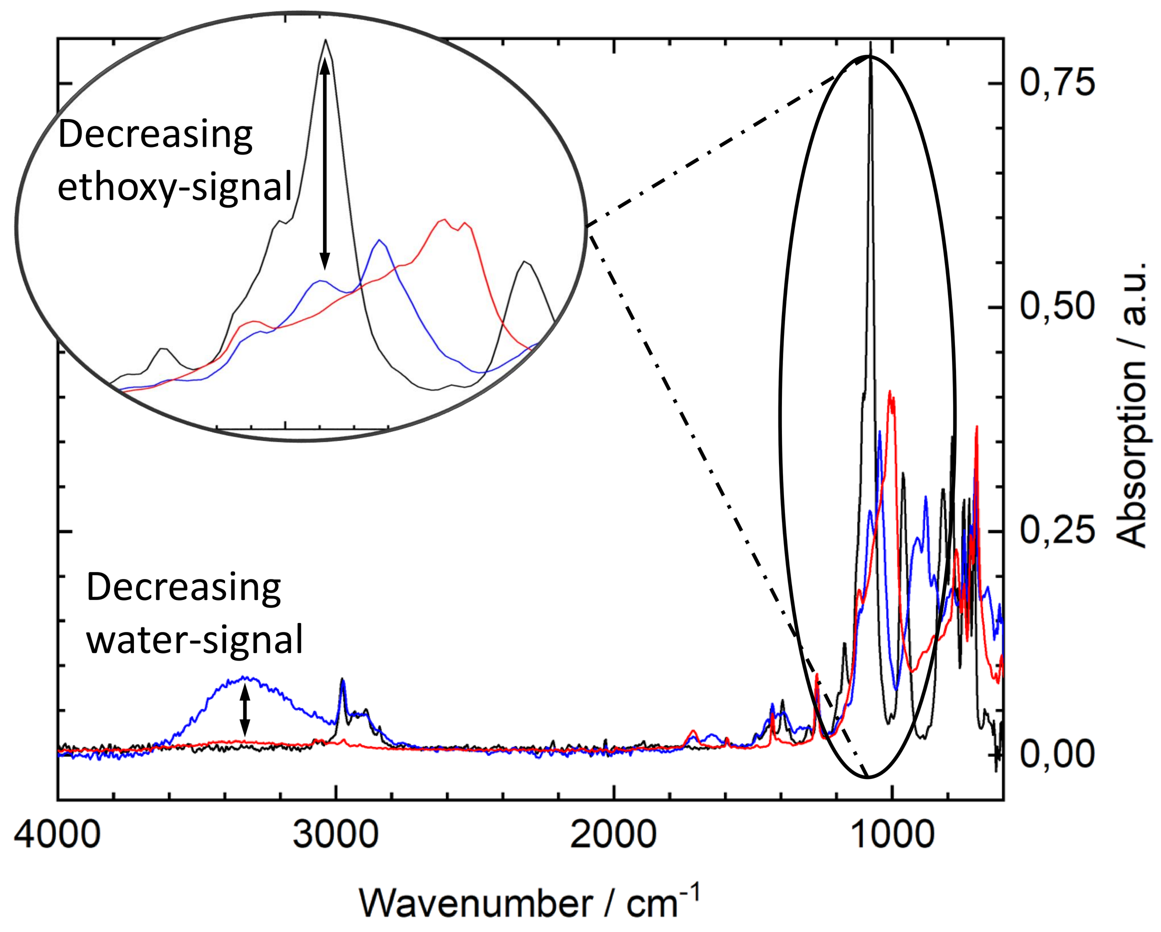

Figure 3: ATR-IR measurements of the silane mixture (black), the reaction solution after turning clear (blue) and the final product (green).

Figure 4 shows the progress measurement with ^{1}H-NMR and Karl Fischer, where the educt concentrations of water, ethoxy, and methoxy groups decrease over time. At first alkoxy-groups are hydrolyzed and the silanol concentration increases until the solution turns clear. Thereafter the amount of silanol groups decreases due to condensation. Additionally, comparison of water determination in the reaction mixture using ^{1}H-NMR and Karl Fischer titration shows a good correlation of both methods.

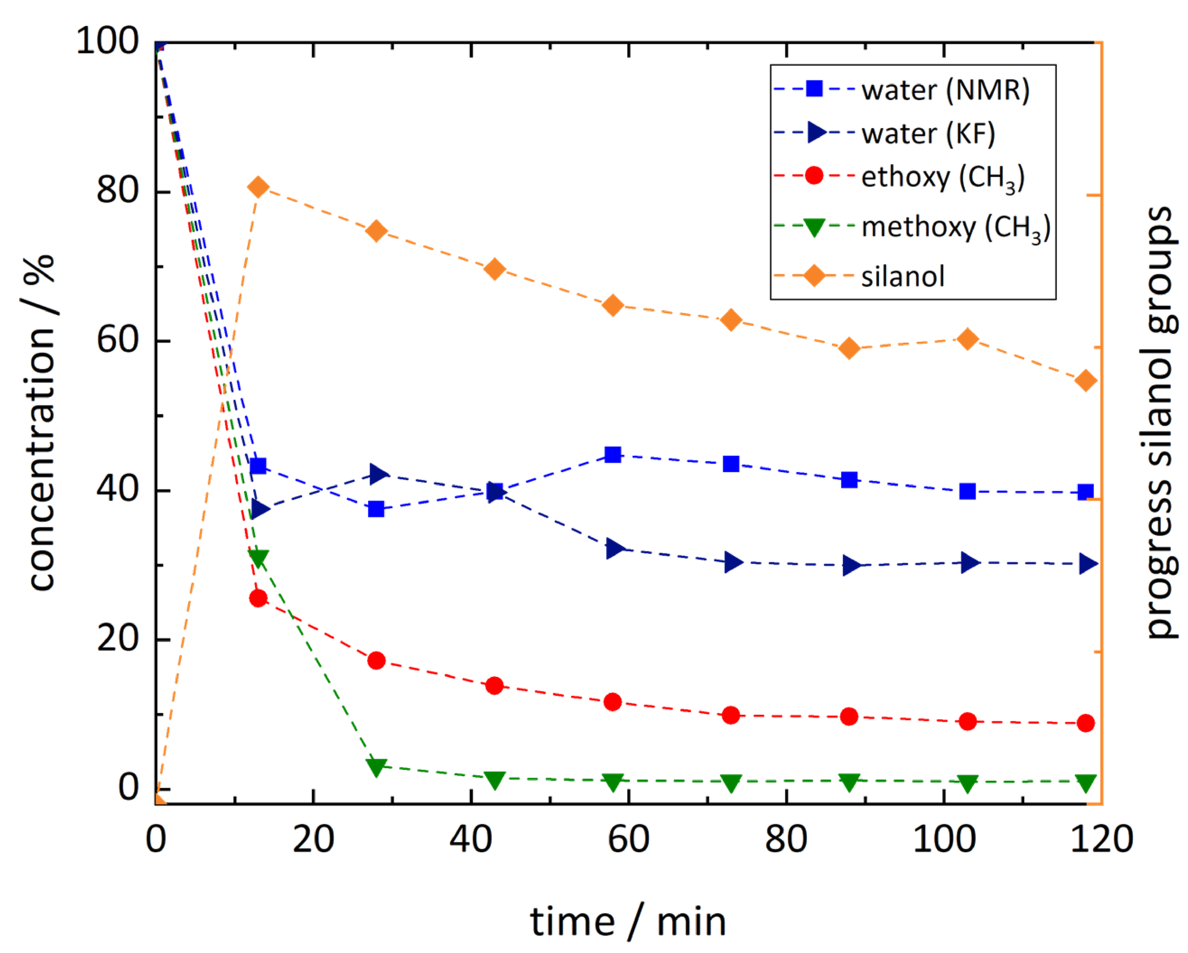

Figure 4: Progress measurement with ^{1}H-NMR of educt- and product concentrations. Results for water concentration compared from ^{1}H-NMR and Karl Fisher (KF) titration.

About the author

Thomas Kisling is currently working on his PhD thesis in the field of coatings based on sol-gel reactions. The focus lies on controlling the structure-properties relationship in sol-gel products.