

The objective of this thesis is to experimentally and numerically investigate the kinetics of sol-gel transition during the synthesis of organoalkoxysilane-based alcogels. The research aims at better understanding of the imposition of chemical reaction and physical phenomena occurring during sol-gel synthesis, such as miscibility gap driven phase separation, polymerization induced phase separation and Brownian motion-driven aggregation. The main goal was to establish analytically a description of gelation kinetics in organoalkoxysilane (methyltrimethoxysilane) based system and to develop a numerical model that would provide an insight into both formation kinetics and gel micro-structure evolution. Nuclear magnetic resonance (NMR) was employed for methyltrimethoxysilane (MTMS) hydrolysis investigation. Experiments were designed to confirm the protonation as the first step of the hydrolysis reaction and to designate its rate constant. Subsequently, the hydrolysis conversion ratio could have been assumed as constant, and the focus of the thesis could be shifted to following the process of organoalkoxysilane gelation.

Further work resulted in development of analytical model describing condensation kinetics, and identification of dominant gelation mechanisms through the three distinguished phases of the process. The dependence of aerogel mass on time was obtained by two methods: spectrophotometrically and by collecting gelled product, deposited on a cellulose filter during the condensation reaction providing additional, quantitative understanding of the organoalkoxysilane gelation.

The thermodynamics of the sol-gel system based on chosen organoalkoxysilanes (methyltrimethoxysilane, vinyltrimethoxysilane and a mixture of co-precursors: methyltrimethoxysilane with dimethyldimethoxysilane) was investigated experimentally by preparation of ternary plots (precursor-solvent-antisolvent) and analysis of polymerization induced phase separation mechanisms – nucleation and growth (N&G) and spinodal decomposition (SD). Based on microstructure analysis performed with scanning electron microscopy, samples could be identified as obtained due to either metastable (N&G) or unstable thermodynamic conditions (SD). Additionally, a ternary plot is an excellent study case for the three-ingredient synthesis, as it provides information about each component's influence on the properties of final structure and kinetics of its formation. Moreover, a new method of analysis of condensation process registered spectrophotometrically was proposed, based on kinetics data interpolation and calculation of first derivative corresponding to the value of condensation rate.

An aggregation model was developed and implemented as a cellular automaton. Model's applicability was verified in terms of providing an insight into gelation kinetics and micro-structure evolution during the sol-gel transition. Based on the interpretation of Arrhenius equation, a novel method of correlation between experimental conditions and model parameters was proposed and validated with experimental data.

This thesis advances the current state of the art with an in-depth and comprehensive understanding of phenomena occurring during the sol to gel transition of organoalkoxysilanes, The results of this thesis enable better prediction of (aero)gels properties, as well as kinetics of gelation, which is especially important while upscaling the synthesis process. The main novelty of this thesis lies in validation of the aggregation model, which was not reported in literature before. Furthermore, dominant mechanisms occurring during condensation phases were identified, providing better understanding of the organoalkoxysilane-based system kinetics.

The presented work is complementary to the one of the current directions of chemical engineering – the synthesis of novel, porous materials that can be tailored for very specific applications, such as silica aerogels. This research proposes and validates the thorough description of organoalkoxysilanes gelation. The determination of kinetic parameters of hydrolysis and gelation is an important step towards upscaling and sustainable synthesis of aerogels.