PhD proposal

Title	Kinetic modelling of nanoporous solid formation in order to control its properties/ Modélisation cinétique de la formation d'un solide poreux

General context:

With the progresses of material science and technology, a variety of nanoporous solids have been employed as adsorbents in chemical processes for environmental protection, energy production and/or purification. Highly cross-linked and transparent hydrogels, as the resorcinol-formaldehyde (RF) aerogel, can be synthesized by sol-gel polycondensation of resorcinol (R) with formaldehyde (F) in a slightly basic (Na_2CO_3) aqueous solution. After a step of drying in supercritical conditions, the cross-linked structure is kept. A RF gel possesses a three-dimensional gel network with numerous mesoporous (2 nm < pore diameter < 50 nm). This polymer is expected to be used as, for example, catalyst support for water decontamination. A precise designing of the porous structure (porosity, tortuosity, specific area, network structure) of such a RF gel is requested to increase the efficiently of the process. Its structure is mostly determined during the sol-gel transition of the RF solution [1,2]. Yamamoto et al. [1,2] measured the transient change of sizes of colloidal particles formed during the sol-gel polycondensation of a RF solution using a Dynamic Light-Scattering (DLS) technique for different resorcinol to catalyst (Na_2CO_3) ratios. They compared the experimental results with a predicted growth rate of colloidal particles using a Population Balance Equation (PBE) simulation model. The simulation fitted well with the experiments results in the early stage of the sol-gel polycondensation but a significant difference between the simulated and the experimental curves have been observed near the gelation time [2]. In this work, we proposed to simulate the formation mechanisms of RF polymer based on the Cahn Hilliard kinetic modelling. This kind of model called "phase field method" in the literature is a successful tool to represent the spinodal decomposition in materials with a composition dependant molar profile and the microstructure evolution typically encountered here. This tool was employed in the Material science to observe the alloy formation [3], polymeric membrane formation [3] or the solidification processes [3, 4].

Aim of the thesis:

The objective of this thesis are:

- to study experimentally the solid phase apparition and the transient change of sizes of colloidal particles formed during the sol-gel polycondensation of a RF solution using a Dynamic Light-Scattering (DLS) technique,
- to model and to simulate this solid phase apparition and its colloid growth in considering the critical physicochemical phenomena as the solid phase apparition, the strongly non-ideality of the solution, the diffusion kinetics of the species in the solution.
- to understand the formation mechanisms of RF polymer and, particularly near the sol-gel transition (coagulation step to form colloids from the clusters), in order to control the polymer characteristics relying on the operating conditions (reactive and catalyst concentration, temperature, pressure, …).

Thesis program

The phD student will be welcomed in the LAGEPP laboratory. The experimental data have been already collected by the University of Hyogo laboratory in a joint collaboration. Several experimental results are available and allows us to follow the colloids and the sol-gel formation of the system relying on several experimental parameters (reactive and catalyst concentration, temperature, pressure, distribution of colloids diameters versus time…). Its thesis program is proposed as follows:

- Carry out a literature review,
- Analyse the collected data by the University of Hyogo and propose new way to insight the mechanisms,
- Add experimental data,
- Model and simulate the formation mechanisms of RF polymer based on the Cahn Hilliard approach.

References	
	[1] T. Yamamoto, M. Tayakout-Fayolle, K. Iimura, H. Satone, T. Kakibe, K. Itoh & K. Maeda, "Effect of high pressure on growth of colloidal particles during sol–gel phase transition of resorcinol–formaldehyde solution," Adsorption, 25, 1115–1120 (2019) [2] T. Yamamoto, S.R. Mukai, A. Endo, M. Nakaiwa, H. Tamon, "Interpretation of structure formation during the sol-gel transition of a resorcinol-formaldehyde solution by population balance," J. Colloid Interface Sci., 264(2), 532–7 (2003). [3] N Moelans, B Blanpain, P Wollants, "An introduction to phase-field modeling of microstructure evolution", Calphad 32 (2), 268-294 [4] C. Ahouré, A. Galfré, C. Cogné, F. Couenne, M. Tayakout, C. Jallut, T. Biben Congrès SFGP2019, France (Nantes)

Profil	
	The candidate will have a background in **chemical engineering**, modelling and simulation. The candidate will have an interest for international collaboration.

Contacts

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