PhD proposal

Title	Experimental study and kinetic modelling of metal ions solution mass transfer in a nanoporous solid / Etude expérimentale et modélisation cinétique du transfert des ions métalliques en solution aqueuse dans un milieu poreux sous gradient de concentration

General context:

With the progresses of material science and technology, a variety of nanoporous solids have been employed as catalysts or adsorbents in chemical processes for energy production, purification and depollution. These processes involve aqueous solution of metal ions in contact with nanoporous solids. For example, certain heterogeneous catalysts are prepared by contacting an aqueous solution of metal ions on a solid support to form chemically nanoparticles [1,2]. In the field of depollution, adsorbents are used to selectively eliminate metal ions contaminating water [3]. The efficiency of these processes depends on the physical and chemical properties of the nanoporous solids and especially their surfaces. To improve the performance of the processes, a better understanding of the mass transfer of ionic species in nanopore, comprising the study of the non-ideality of the ionic solution, adsorption and precipitation phenomena on the solid surface under concentration gradient, needs to be performed. The level of knowledge in the field is largely incomplete, although it is of major interest for various industrial applications.

Aim of the thesis:

The objective of this thesis is to study experimentally and theoretically the diffusion, adsorption and precipitation of ionic aqueous media in porous solids, taking into account the critical physicochemical phenomena that are:

- The strongly non-ideality of the aqueous phase thermodynamic equilibria, in particular at high ionic strength and the influence of this non ideality on adsorption and diffusion steps.
- The impact of the physicochemical properties of the surface on adsorption and diffusion.
- The influence of confinement of molecules on phase equilibria in meso and micro porous systems.
- The ionic specie diffusion in nanoporous solid.

Thesis strategy:

The scientific problematic being particularly complex, we propose to limit the study to a simple but relevant system in the field of heterogeneous catalyst: the interaction between metal ions and the surface of gamma alumina. The heterogeneous catalyst preparation consists on the deposition of metal nanoparticles on a solid support which forms the active phase of the adsorbent. The adsorbent is brought into contact with an aqueous solution containing the metal precursor. The ionic species are adsorbed on the surface of the solid, according to a thermodynamic equilibrium which depends on the operating conditions (temperature, concentration, pH, ionic strength, physicochemical properties of the surface), before forming nanocrystals by precipitation.

The study will be performed by decoupling as much as possible the different phenomena and by stages of increasing complexity.

- The first part of the study will be carried out at a low concentration in order to avoid the salts precipitation. Under these conditions, the equilibrium behaviour of the fluid phase and the adsorbed phase will be measured and modelled, as well as the diffusion kinetics in the porous network of the solid.
- In a second time the precipitation phenomena will be undertaken. The main objective will be to evaluate the impact of pore size (confinement) on the size and morphology of the metal nanoparticles.

Thesis program

The phD student will be welcomed in the LAGEPP Laboratory. Its thesis program is proposed as follows:

- Carry out a literature review
- Develop data analysis tools to follow the different ionic species in solution on line and the precipitated forms on the solid surface out of line
- Study the catalyst impregnation (adsorption, solid deposit and precipitation of nickel ions) under different conditions of nickel, pH and ionic force in continuous stirred tank reactor, based on reversed-phase chromatography method (breakthrough experiments by adding salt or acid).
- Measure and model the fluid phase equilibria.
- Study of salt precipitation by a controlled evaporation of water.
- Begin the modelling of the mass transfer, phase apparition and growing of the solid on the solid surface by phase field method.

Results valorisation

The theoretical and experimental methodologies developed during this thesis will be useful for other applications. For example, the results of this work will be used to remove cesium ion efficiently from the aqueous solution [4] employing porous materials. Indeed, this subject has been of great interest after the serious accidents of nuclear power plants in Japan and it will be done in collaboration with T. Yamamoto (Professor of University of Hyogo.) An extension of this work to ion mixtures can be of great interest in the field of heterogeneous catalysts impregnation.

References

[1] K.-M. Hong, M.-S. Kim and J. G. Chung Chemosphere 54 (2004) 927–934 doi:10.1016/j.chemosphere.2003.08.036
[2] S. Malamis, E. Katsou Journal of Hazardous Materials 252– 253 (2013) 428– 461 doi : http://dx.doi.org/10.1016/j.jhazmat.2013.03.024
[3] C. Jeon, J-O Kim and Seung-Mok Lee. Korean Journal of Chemical Engineering. 31. (2014). 1219-1224. Doi: 10.1007/s11814-014-0058-7.
[4] C. Dwivedi, A. Kumar, J.K. Ajish, K.K. Singh, M. Kumar, P.K. Wattal and P.N. Bajaj, RSC Advances 2 (2012) 5557-5564 DOI: 10.1039/c2ra20054f

Profil

The candidate will have an initial background in analytical chemistry and a strong interest in multidisciplinary research (On-line analysis, chemical engineering, modelling and simulation)

Contacts

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