Porous capsules with liquid core prepared by Pickering emulsion: Understanding of diffusional phenomena for catalyst implementation.

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Résumé

The ideal catalyst is likely to merge the advantages of both homogeneous and heterogeneous catalysis. For example, it may exhibit the performance of a homogeneous catalyst in terms of activity and selectivity combined with the ease of use of a heterogeneous catalyst. In that context, the possibility to entrap a homogeneous phase catalytic system within a solid porous capsule would lead to a system that allows the catalytic performances to be maintained under certain conditions, with a material that is easy to handle. Therefore, the conditions for maintaining its performances lie partly in the efficiency of diffusional transfers:
- The transfer of reagents from the external medium (phase immiscible with the internal phase of the capsule) to the interior of the capsule. This transfer takes place via a solid medium which constitutes the capsule shell.
- The transfer of the reaction products from the liquid phase inside the capsule (phase immiscible with the phase outside the capsule) to the outside of the capsule.
- The transfer of the catalytic system from a liquid phase inside the capsule to an immiscible phase on the outside via the shell. This phenomenon must be absolutely limited to maintain the catalytic activity.

Such type of material can be obtained from a Pickering emulsion (emulsion stabilized with solid nanoparticles), where the dispersed phase is a homogeneous phase catalyst. Then, in order to prepare liquid filled microcapsules, shell consolidation can be achieved by sol-gel process to create a metal oxide (such as SiO2) porous wall allowing reagents and products to diffuse easily.

*Intervenant

Here, we describe the design of such material obtained by a Pickering emulsion using hydrophobized silica nanoparticles with ionic liquids ((BMIM)(NTf2) and (BMIM)(BF4)), water and a catalyst (HNTF2) as the dispersed phase and heptane as the continuous phase. These ionic liquids and this catalyst have been chosen in order to carry out the isobutene dimerization reaction, which is the model reaction chosen for this project because it is well mastered by IFPEN. The final capsules are formed from the emulsion droplets by hydrolysis of alkoxysilanes and polycondensation of the resulting products. Those capsules have been studied using optical microscopy, scanning electron microscopy (SEM), confocal microscopy, nitrogen sorption and mercury porosimetry. The main difficulty lies in characterising the capsules: Indeed, once the sol-gel process is complete, the capsules must remain in suspension to be used for the model reaction. This is a source of concern regarding the evaluation of certain characteristics like textural properties impacting diffusion. Indeed, the material needs to be dried to perform nitrogen sorption or mercury porosimetry. When dried, silica gel is subject to shrinkage, which completely changes its textural properties. The results obtained using mercury porosimetry or nitrogen sorption therefore do not represent the real system. However, it is possible to obtain the real porosity and pore size distribution of capsules still in liquid using a less common method: thermoporometry, which is a calorimetric method for characterizing pore structure from the melting or freezing point depression of a liquid confined in a pore.

A washing protocol has been developed to extract all the substances contained in the capsules, particularly the ionic liquids. This included successive washes with methanol and heat treatment at 390∘C under nitrogen to decompose the ionic liquids remaining after the washes, while limiting densification of the silica gel due to dehydroxylation and decomposition of silanols, leading to polycondensation. The first capsules synthesised had intermediate type II/type IV isotherms with a hysteresis loop that starts at high pressure (reflecting the presence of large mesopores) and ends at around 0.42 (reflecting the presence of small mesopores). The BET specific surface area obtained varies between 200 and 250 m^2/g, the mesoporous volume between 0.4 and 0.45 cm3/g and the microporous volume between 0.05 and 0.1 cm3/g. The DFT pore size distribution shows peaks in micropores area at 1.4 and 1.7 nm and peaks in mesopores area at 4 and 50 nm. These results were confirmed using the BJH model for mesopores and the HK model for micropores. These capsules have a multiscale porosity: microporosity, mesoporosity and mercury porosimetry confirmed that there is even macroporosity. However, textural properties of silica gel forming the shell of these capsules are highly dependent on experimental conditions, including pH, molar ratio of water to alkoxysilane, type and functionalisation of the alkoxysilane and temperature.
The diameter of the capsules depends on that of the Pickering emulsion droplets which varies according to the speed of agitation during emulsification and the quantity of nanoparticles introduced. Capsules ranging from 10 μm to 50 μm were obtained using an Ultraturrax. Capsules' shell is very thin (approximately 50 nm), which results in very low mechanical strength (the capsules crush on themselves or break very easily). The textural properties, size and thickness of the capsules have an influence on diffusion, so it's important to master them.