DESIGNING NANOPOROUS MATERIALS FOR CATALYSIS

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In the last decade, the great development of ordered mesoporous materials has attracted much attention. Their excellent properties: high surface area, narrow pore size distribution and tunable porous network and connectivity, are leading to broaden the limits of applications of nanoporous solids as catalysts, adsorbents and catalysts carriers. However, for certain catalytic applications, the typically amorphous nature of the walls (framework) in these mesoporous materials is a drawback. Based upon what is known about zeolite chemistry, different synthesis strategies have been developed in order to improve framework ordering in mesoporous materials [1, 2]. From a different approach, a very promising field has been established taking advantages of the high density of surface silanol groups inside mesoporous silica networks. Being these surface silanol groups anchoring centres for functional alcoxysilanes (usually organosilanes), they therefore turn into potential tailor-made shape selective catalysts for bulkier molecules [3-5]. Nowadays, the porous structures can be fine tuned controlling the synthesis conditions leading to ordered mesoporous materials with cage-type of systems. For certain fine chemical synthesis and biosensing applications, these materials are thought to be very useful supports since it would be desirable to encapsulate bulky enzymes in independent cavities, connected by pores of tuned size, solving therefore problems related to diffusion, aggregation, leaching, and conformation [6].

In its early stages, ordered mesoporous materials synthesis was based on a similar approach to that of crystalline zeolites, that is, hydrothermal treatment of silicate/ aluminosilicate gels containing large surfactant molecules. In zeolite synthesis, a simple organic molecule acts as a template creating highly crystalline materials with well defined pore space. However, this "templating effect" is nowadays explained based mainly on experimental observations. Understanding the interactions and driving forces in the synthesis of zeolites with structure directing agents (SDA) would allow a real design of both, the pore space and the distribution of heteroatoms along the inorganic framework. Recently, we have extensively used computational studies coupled with experimental work in order to tailor the zeolite synthesis and the introduction of heteroatoms in the zeolitic framework. It has been demonstrated that fluorine improves the templating ability of certain molecules, as compared with the all-hydrogen counterpart. A computational study of the interaction between the different cations and the inorganic framework has allowed explaining the experimental results in terms of the packing efficiency and interaction energies of the molecules inside the channels [7-9].

In the same direction, the self-assembly mechanism involved in the synthesis of ordered mesoporous materials is still unknown. The pore space is thought to be the replica of the liquid crystalline phase of the corresponding surfactant. However, nowadays the surfactant chemistry applied in this synthesis is becoming more complicated by adding inorganic salts and organic additives. Furthermore, when silica is added to a water/surfactant system, the silica hydrolysis and condensation kinetics at certain pH plays a key role in the resulting structure. Thus, the nature of the interactions surfactant-inorganic precursors that governs the formation of ordered mesoporous materials, and above all its effect in the final structure, is rather unclear. In these cases, *in situ* techniques have shown to be a promising route to provide information about the organic-inorganic interface. More specifically, we are applying *in situ* infrared spectroscopy (ATR-FTIR) to follow the kinetics of the sol-gel synthesis of

nanoporous molecular sieves in a stirred reaction vessel adapted to a horizontal attenuated total reflectance (ATR) accessory. Diamond has been chosen as internal reflection element because of the hardness, thermal and chemical resistance requirements that the synthesis conditions impose. The use of this tool to analyse the formation of the surfactant-silicate mesophase and monitor the hydrolysis and condensation reactions during the synthesis of MCM-41 materials has been reported [10].

Finally, Scanning (SEM) and Transmission (TEM) Electron Microscopy, and related techniques, are currently used to elucidate the morphology and nature of the nanoporous structure along with heteroatom distribution. In general terms, SEM provides the morphology information and TEM allows identifying the internal structure within the crystals. In these cases, a reliable statistic TEM/EDX (Energy Dispersive X-ray Spectroscopy) study provides chemical composition information at nanometer scale that can be correlated to bulk inorganic composition estimated by other techniques. This comparison, rarely presented in the literature of nanoporous materials, would indicate whether the heteroatom distribution is homogeneous or not. One has to bear in mind that a TEM image is a two-dimensional output of a three-dimensional object, i.e., a projection of the volume along certain direction. Thus, TEM images along different orientations of the same crystal (tilting series) are usually helpful and required prior to any nanoporous structure assessment. More specifically, Selected Area Electron Diffraction (SAED) patterns coupled with High Resolution Transmission Electron Microscopy (HRTEM) images constitute a powerful tool to analyze the evolution of the crystalline structure along with the control of a desirable morphology in nanoporous materials [11-14].

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