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The first direct probing of porosity on supported mesoporous silica thin films through hyperpolarised ^{129}Xe NMR†

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The continuous flow hyperpolarised (HP) ^{129}Xe NMR technique has been used for the first time on mesoporous silica thin films. This study demonstrates the possibility of recording information about the porosity of a very small quantity of materials and the high sensitivity of the NMR response to pore size and pore functionality.

The field of mesoporous materials has experienced increased interest in the last decade following the introduction of the supramolecular template approach by Beck and co-workers.[1] The evaporation-induced self-assembly (EISA)[2] process represents an interesting way to design mesostructured organic–inorganic hybrids, which are precursors for mesoporous solids. By this process, silica[3,4] and non-silicate[5] based mesoporous materials have been prepared as thin films. Silica films are transparent, exhibit good mechanical stability and they can therefore be directly used in optical devices, sensors, membranes, *etc*. However, one of the main problems of these mesoporous thin films is related to the characterisation of their porous structure (pore size; pore volume). Cross-techniques such as TEM, XRD and adsorption isotherms are very useful to gain a maximum of relevant and accurate data about the porous network, its accessibility and its connectivity. In mesoporous thin films the porosity can be estimated by nitrogen adsorption isotherms; however this technique requires either to scratch off a few tens of samples from their substrates or to perform the analysis within a home made cell that can accommodate a large set of thin films.[6] Such measurements which are time consuming present additional drawbacks: the information is averaged over several films and the error on the sample weight is large, especially when scratching the films, since substrate pieces can be mixed with the sample.

In the past twenty years, ^{129}Xe NMR has become a popular technique for the characterisation of porous solids.[7,8] However, application of thermally polarised ^{129}Xe NMR to materials is often hampered by a relatively weak signal due to low concentration of adsorbed xenon and long relaxation times (this is particularly the case for mesoporous silica[9]). An increase in sensitivity of several orders of magnitude ($\times 10^4$) can be achieved by using optical pumping techniques for the production of hyperporalised (HP) xenon,[10] which have made it very attractive for materials applications[11] and should allow very small quantities of matter to be probed.

Here we report for the first time the direct probing of thin supported films of mesoporous silica. This first application of continuous flow hyperpolarised (HP) ^{129}Xe NMR to porous films is of paramount importance because it opens a land of opportunities for the *in situ* characterisation of porous materials deposited as thin films on any given device.

The mesoporous silica thin films were prepared *via* the sol–gel chemistry process[4] (ESI†). After thermal treatment at 350 °C aimed at strengthening the inorganic framework and eliminating the organic surfactant, the silica film was characterised by 2D small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) performed on the film cross-sections (Fig. 1).

These results show that the film has a 3D hexagonal structure corresponding to the $P6_3/mmc$ space group.[4] The whole film is well organised and mono-oriented with the *c* axis normal to the substrate surface (see Fig. 1). The spherical pores have a diameter of ~25 Å as evaluated from TEM measurements. Such a material displayed a high surface area (about 1000 m^2 g^{-1}) which was measured with the N_2 adsorption–desorption isotherms technique on the powder obtained from several scratched films. The estimated pore size range between 20 Å and 30 Å depending on the model (BJH, DFT,...) used to fit the isotherm data.

Six slices of the supported silica films were cut into 0.3×1.5 cm^2 pieces, which represent 0.1 to 0.2 mg of mesoporous silica. They were placed into 8 mm NMR tube with 2 stopcocks for delivering a flow of HP xenon, heated in vacuum to 400 °C (at 60 °C h^{-1}) and kept at this temperature for 12 h. After that the sample was attached to the continuous flow system *via* 1/8" plastic tubing and placed into the NMR probe.

The continuous flow system for production of hyperpolarized xenon based on the design of ref. 12 has been described elsewhere (ESI).† Fig. 2 shows the variable temperature ^{129}Xe NMR spectra of HP xenon adsorbed on the supported mesoporous silica film. The intense line at 0 ppm in all of these spectra is related to xenon in the gas phase. This NMR signal is the only one observed in blank experiments performed with the glass slides at different temperatures (from RT to 143 K) and different Xe pressures.

When mesoporous films are deposited on the glass slides a second signal located at low field due to adsorbed xenon appears. At room temperature the spectrum displays a broad asymmetric line with a maximum at *ca.* 25 ppm and a linewidth of *ca.* 4 kHz. The decrease in temperature leads to a shift of the line from adsorbed xenon to lower field and to narrowing of the

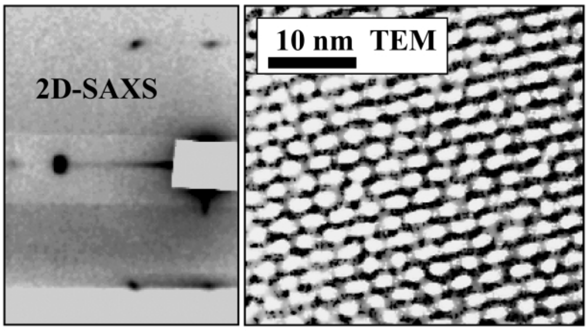

Fig. 1 2D Small angle X-ray scattering (SAXS) pattern recorded at grazing incidence on a mesoporous silica thin film and the corresponding transmission electron microscopy (TEM) image.

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† Electronic supplementary information (ESI) available: materials, NMR measurements, modification of silica surface. See http://www.rsc.org/suppdata/cc/b2/b207127d/

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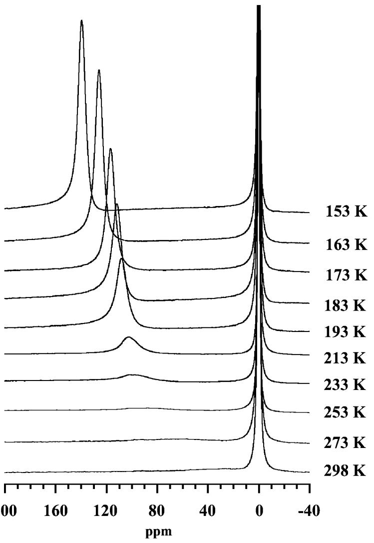

Fig. 2 Variable temperature HP ^{129}Xe NMR spectra of xenon adsorbed on silica mesoporous films.

signal (to *ca.* 0.5 kHz at 163 K). The intensity of these lines notably increases with decreasing temperature due to increased adsorption of xenon.

In general, there exist empirical relationships between the dimensions of the voids and xenon chemical shifts for zeolites and mesoporous materials.[13] The obstacles and limitations of such an approach have been explored in several papers.[13,14] In our case, the signals observed at room temperature and just below are very different from those observed in the case of mesoporous powders,[11,14] which are typically much narrower. The reasons for such a broad signal at room temperature may be a distribution of pore diameters, poor organisation of the mesoporous phase and/or the exchange process between xenon adsorbed in the pores and on the outer surface of the film. The first two explanations can be ruled out since TEM and XRD data (*vide supra*) show quite a narrow distribution of pore sizes and a high degree of ordering of the mesoporous structure. As for the exchange phenomena, they are known to be responsible for broadening of NMR signals of ^{129}Xe in mesoporous powders in the case of small particle dimensions (< 10 μm) due to the formation of an interparticle secondary pore system. In our case, such a severe broadening is not possible, since these mesoporous continuous films are free of interparticle pores. The observed broadening could thus be attributed to the presence of shallow mesopores, in which xenon atoms are not confined, but spend part of their time in the outer space. (Actually, this phenomenon might be partially responsible for the observed exchange broadening of the lines in mesoporous powders too.) When the temperature decreases, exchange with the gas phase drastically diminishes and the observed chemical shift becomes a function of the chemical composition of the surface and of the Xe–Xe interactions in the adsorbed layer. The evolutions of the xenon chemical shift values with temperature in compressed MCM-41 powders and in film (Fig. 3) illustrate these ideas. The changes in chemical shifts with temperature for both samples are quite similar in the low temperature region ($T < 250$ K), where the shifts are mostly dependent on the chemical nature of the surface, which should not be very different between the powders and the films. At ambient temperature and just below, the exchange processes in the film play an important role which leads to pronounced differences.

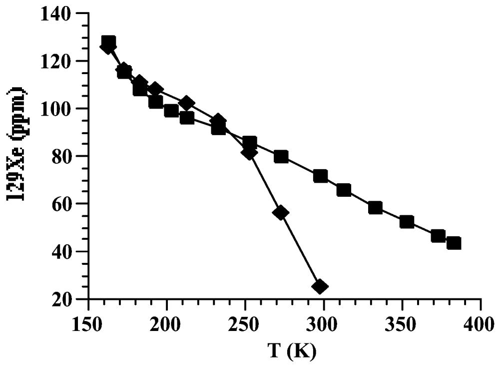

Fig. 3 Evolution of the ^{129}Xe NMR chemical shifts *vs.* temperature for porous silica materials: ■ compressed MCM-41 powders; ◆ mesoporous silica film.

In summary, the data presented here clearly show that the porosity of thin films can be probed directly by using HP ^{129}Xe NMR and the pore size can be estimated from the observed variations of the chemical shift of adsorbed xenon *versus* temperature. Moreover, important variations of the NMR response are obtained on organically functionalised silica hybrid film demonstrating the very high sensitivity of this technique to probe surface modifications in porous films (ESI†).

However, these very promising results must be improved in the future through a systematic study of films with different structures and functionalities. A thorough analysis and modelling of the data would lead to quantitative pore size evaluation and connectivity description of mesoporous thin films.

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