Kinetics of polycondensation reactions during self-assembly of mesostructured films studied by *in situ* infrared spectroscopy†

Plinio Innocenzi,*[a] Luca Malfatti,[a] Tongjit Kidchob,[a] Paolo Falcaro,[b] Mariangela Cestelli Guidi,[c] Massimo Piccinini[c] and Augusto Marcelli[c]

Received (in Cambridge, UK) 9th December 2004, Accepted 28th February 2005
First published as an Advance Article on the web 18th March 2005
DOI: 10.1039/b418381a

***In situ* synchrotron FTIR experiments have been performed during evaporation-induced self-assembly (EISA) of mesoporous films and the role of silica polycondensation in obtaining highly organized mesostructures has been illuminated.**

The organization through evaporation-induced self-assembly (EISA)[1,2] of mesostructured silica materials is given by a delicate balance of different processes in competition with each other. The so called "race towards order"[3,4] successfully results in an organized structure only if the kinetic constants involved in the process follow this hierarchy:

$$k_{\mathrm{inter}} > k_{\mathrm{org}} > k_{\mathrm{inorg}} \qquad (1)$$

where k_{inter}, k_{org}, and k_{inorg} are respectively the relative rates for interface formation, organic array assembly, as it exists in the final mesostructure configuration, and silica polycondensation.

On the other hand, the inorganic or hybrid bricks used to build up the pore walls of mesoporous materials are synthesised using sol-gel chemistry which has to be combined with the micelle organization and the formation of an interface between the bricks and the surfactant. At low pH conditions (pH $\approx$ 2), the silica reactivity is slow enough for supramolecular units (micelles) to organize before a rigid network is formed. In the preparation of mesostructured films, the evaporation rate of the solvent must be controlled for self-organization[5,6] to occur. Although the general theory of EISA is well understood, there is still a lack of experiments to support it. We have performed a simple *in situ* experiment using infrared synchrotron radiation to study the kinetics of silica condensation during EISA. The synchrotron infrared beamline at DAΦNE (SINBAD) in the Laboratori Nazionali (Frascati, Italy) of the Istituto Nazionale di Fisica Nucleare (INFN) was used for the experiments. The IR radiation is extracted from a bending magnet of the electron ring and transmitted to an interferometer at a distance of about 25 m. The beamline is kept under ultra-high vacuum up to the diamond window placed at the entrance of the interferometer which is a Bruker equinox 55 modified to work down to 10^{-2} mbar. The measurement was done in air *via* transmission mode with a Bruker IR microscope that was installed laterally with respect to the interferometer. Mid-IR measurements were performed using the interferometer working in vacuum, in the range 500–6000 cm^{-1} and with a resolution of 4 cm^{-1}. The advantage of the experimental configuration that we have adopted is that we can record transmission spectra with good signal-to-noise (S/N) ratio at time scales short enough to investigate the kinetics of the reactions involved during EISA of films. Infrared synchrotron radiation is certainly comparable with a standard source in the mid-infrared region but more brilliant (up to a factor of 4 to 5 in this energy range at SINBAD). In this case working with a microscope it may be a significant advantage for experiments where kinetics and S/N ratio may be crucial. An MCT detector (1 mm^2 size) cooled to the nitrogen temperature and a KBr beam splitter were used.

The IR spectra were recorded with an interval of 3 seconds. Diamond was selected as substrate because of the excellent transmission in the 700–2000 cm^{-1} region. A series of systematic experiments with increasing amounts of solutions, up to 50 μl per drop, were previously performed to select the volume of solution to be cast.

Larger volumes of solution cast on the diamond disk gave, in fact, saturation of the spectra, or the kinetics was too slow to simulate a film formation. A small drop of the sol (2 μl) was cast on a diamond disk; immediately after, the kinetics of solvent and water evaporation, together with silica polycondensation, were followed *in situ* by FTIR. We have also correlated the measured kinetics with the order of the final material by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) measurements (see supplementary information 1 and 2).[7] Four different sols were prepared for these experiments: (1) tetraethyl orthosilicate (TEOS), H_2O, EtOH, HCl; (2) TEOS, H_2O, EtOH, HCl and $H(C_2H_4O)_{106}$–$(C_3H_6O)_{70}$–$(C_2H_4O)_{106}H$ (Pluronic F127 block copolymer); (3) TEOS, methyltriethoxysilane (MTES), H_2O, EtOH, HCl; (4) TEOS, MTES, H_2O, EtOH, HCl and Pluronic F127. Molar ratios were set as follows: TEOS : (MTES) : EtOH : H_2O : HCl : (F127) = 1 : (0.56) : 24.48 : 14.70 : 0.11 : ($7.6\cdot10^{-3}$). During our experiments we observed that sol (4) gives a highly reproducible self-assembled porous mesostructure in comparison with sol (2) (see supplementary information 1).

The *in situ* IR spectra measured during EISA, detected at intervals of 3 seconds, are shown in Figs. 1 (TEOS–MTES systems) and 2 (TEOS systems).

The spectra of a reference sol, prepared without the organic template, allow a direct comparison of the effects of surfactant on kinetics of the processes involved in EISA.

We have used the 1640 cm^{-1} vibrational mode to follow the change in water content in the films (insets in Figs. 1 and 2). The results show that the trend is similar for all the systems and is

---

† Electronic supplementary information (ESI) available: TEM and SAXS images. See http://www.rsc.org/suppdata/cc/b4/b418381a/
*plinio@uniss.it

This journal is © The Royal Society of Chemistry 2005

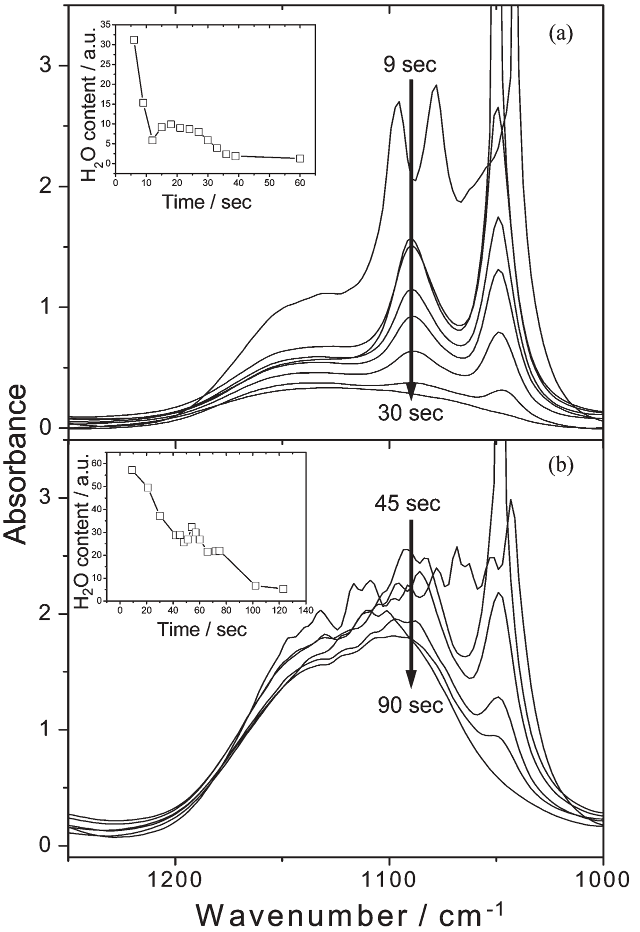

Fig. 1 Infrared absorption spectra recorded at different times after film deposition for (a) TEOS–MTES and (b) TEOS–MTES–F127 systems. The variation of water content in the films, measured by the change in absorption area of the 1640 cm^{-1} band, is shown in the Figure insets.

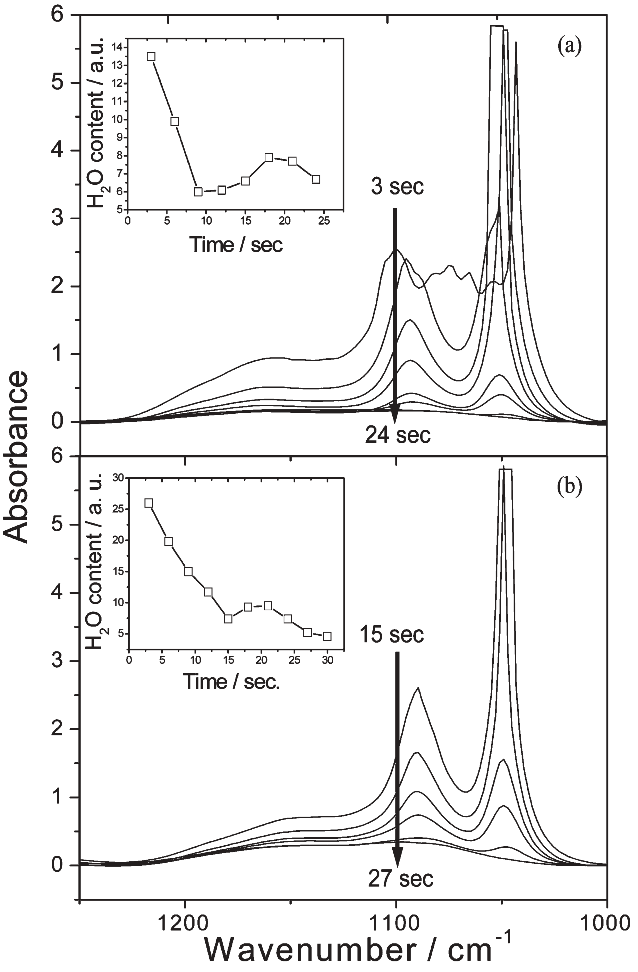

Fig. 2 Infrared absorption spectra recorded at different times after film deposition for (a) TEOS and (b) TEOS–F127 systems. The variation of water content in the films, measured by the change in absorption area of the 1640 cm^{-1} band, is shown in the Figure insets.

related to sol-gel chemistry of film formation.[8–10] An initial rapid evaporation is followed by a small increase in water content, in correspondence with silica polycondensation reactions, and a second evaporation stage. These results are not obvious as few authors, to explain EISA, were taking into account the real evolution of water content as a function of time. However, as we show here, the water evaporation can be modeled using three different phases: (a) Fast Initial Evaporation (FIE); (b) Water Enrichment (WE) due to silica polycondensation and (c) Second Evaporation Stage (SES). After SES, however, not all the water is evaporated from the as deposited films, as clearly observed by the infrared spectra (not shown in the Figures).

It is important to observe that, even if the trends in the four systems are the same, the evaporation times are different: the FIE phase slowed with presence of the surfactant.

The kinetics of silica polycondensation has been followed observing the IR transmission in the 1000–1250 cm^{-1} range. The first spectra are dominated by the strong signature of ethanol vibrational modes (1044 and 1095 cm^{-1}).[11] The rapid evaporation of alcohol (*vide infra*) creates a water-rich film and pushes the polycondensation reactions to form the silica network. The condensation rate of silica can be estimated using the Si–OC_2H_5 vibrations in TEOS and MTES as references. The unreacted alkoxides give rise to absorption bands at 1096 cm^{-1} (ν_{as} (C–O)) and 1048 cm^{-1} (ν_s (C–O)).[12] To calculate the differences in the kinetics, we have assumed as a reference the moment when the 1048 cm^{-1} band is no longer detected. At this point only the main ν_{as} (Si–O–Si) vibrational mode around 1100 cm^{-1} due to silica[11] is observed.

The IR results show, therefore, that there is a significant trend also in the case of silicon alkoxides reaction kinetics. The presence of the surfactant slows down the silica polycondensation and this effect is crucial in the MTES–TEOS–F127 system. On the basis of these results, we can explain the much increased tendency to form highly organized mesostructures during EISA. A slower rate of polycondensation gives, in fact, more time for the micelles to organize before a rigid network is formed and/or phase separation is observed.

A comparison between the different kinetics of ethanol and water evaporation during EISA can be obtained from FTIR spectra using a 2D correlation analysis.[13] Fig. 3 shows the asynchronous spectra‡ obtained correlating in 2D the absorption spectra of MTES–TEOS–F127.

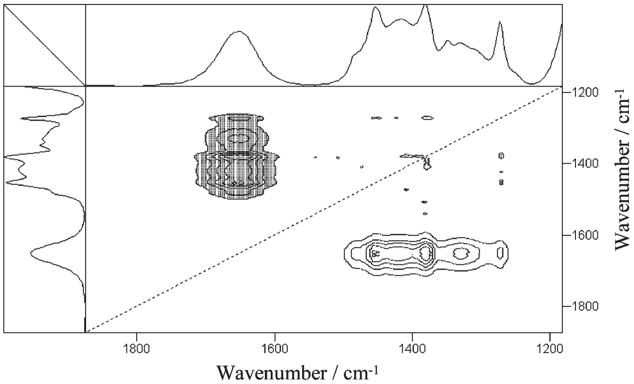

Fig. 3 Asynchronous 2D IR correlation spectrum of MTES–TEOS–F127.

The two symmetric cross peaks out of diagonal are respectively negative (shaded area) and positive showing the time correlation between ethanol and water. The presence of a positive cross peak of ethanol around 1400 cm^{-1}, which is large because of the several overlapped bands due to ethanol in this interval, means that the intensity change of ethanol occurs predominantly before that of water at 1640 cm^{-1}.

Our experiments show that the evolution of silica condensation, which is within a few tens of seconds, is not negligible to explain EISA as supposed by other authors.[14,15] The silica polycondensation rate is, instead, a basic parameter to be taken into account during EISA: the IR measurements show, in fact, that longer polycondensation kinetics, even in this short time scale, give a better and easier organized mesostructure.

In summary we have performed *in situ* FTIR measurements to investigate the kinetics of processes involved in EISA of films. The evaporation of water is observed to take place in three different phases, with a first rapid evaporation followed by an increase in H_2O content and a second evaporation stage. The polycondensation of silica is highly slowed down in presence of hydrophobic methyl groups, resulting in a very high degree of order in the final mesostructure.

FIRB Italian projects are acknowledged for financial support (FIRB contract no. RBNE01P4JF).

Plinio Innocenzi,*[a] Luca Malfatti,[a] Tongjit Kidchob,[a] Paolo Falcaro,[b] Mariangela Cestelli Guidi,[c] Massimo Piccinini[c] and Augusto Marcelli[c]
[a] *Laboratorio di Scienza dei Materiali e Nanotecnologie, Nanoworld Institute, Dipartimento di Architettura e Pianificazione, Università di Sassari, Palazzo Pou Salid, Piazza Duomo 6, 07041, Alghero (Sassari), Italy. E-mail: plinio@uniss.it; Fax: +39 079 9720408; Tel: +39 0799720420*
[b] *Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, Via Marzolo 9, 35131, Padova, Italy*
[c] *Laboratori Nazionali di Frascati – INFN, Via E. Fermi 40, 00044, Frascati, Italy*

Notes and references

‡ 2D correlation spectra were obtained using the 2D-Pocha program by Ozaki *et al.* available at http://sci-tech.ksc.kwansei.ac.jp/~ozaki/2D-Pocha.htm.

1 C. J. Brinker, Y. Lu, A. Sellinger and H. Fan, *Adv. Mater.*, 1999, **11**, 579.
2 G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093.
3 Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.
4 G. J. de A. A. Soler-Illia, E. L. Crepaldi, D. Grosso and C. Sanchez, *Curr. Opin. Colloid Interface Sci.*, 2003, **8**, 109.
5 P. Innocenzi, P. Falcaro, D. Grosso and F. Babonneau, *J. Phys. Chem. B*, 2003, **107**, 4711.
6 P. Falcaro, D. Grosso, H. Amenistch and P. Innocenzi, *J. Phys. Chem. B*, 2004, **108**, 10942.
7 P. Falcaro, S. Costacurta, G. Mattei, H. Amenitsch, A. Marcelli, M. Cestelli Guidi, M. Piccinini, A. Nucara, L. Malfatti, T. Kidchob and P. Innocenzi, *J. Am. Chem. Soc.*, 2005, DOI: 10.1021/ja0427956.
8 C. J. Brinker, G. C. Frye, A. J. Hurd and C. S. Ashley, *Thin Solid Films*, 1991, **201**, 97.
9 F. Nishida, J. M. McKiernan, B. S. Dunn, J. I. Zink, C. J. Brinker and A. J. Hurd, *J. Am. Ceram. Soc.*, 1995, **78**, 1640.
10 M. H. Huang, H. M. Soyez, B. S. Dunn and J. I. Zink, *Chem. Mater.*, 2000, **12**, 231.
11 P. Innocenzi, *J. Non-Cryst. Solids*, 2003, **316**, 309.
12 H. Yoshino, K. Kamiya and H. Nasu, *J. Non-Cryst. Solids*, 1990, **126**, 68.
13 I. Noda and Y. Ozaki, *Two-Dimensional Correlation Spectroscopy—Applications in Vibrational and Optical Spectroscopy*, 2004, John Wiley & Sons, Chichester, England.
14 F. Cagnol, D. Grosso, G. J. de A. A. Soler-Illia, E. L. Crepaldi, F. Babonneau, H. Amenitsch and C. Sanchez, *J. Mater. Chem.*, 2003, **13**, 61.
15 D. A. Doshi, A. Gibaud, V. Goletto, M. Lu, H. Gerung, B. Ocko, S. M. Han and C. J. Brinker, *J. Am. Chem. Soc.*, 2003, **125**, 11646.

This journal is © The Royal Society of Chemistry 2005