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Reviews

In Situ Studies of the Sol−Gel Synthesis of Materials

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The use of in situ methods to study the synthesis of materials from sol−gel precursors is reviewed, with particular emphasis on the formation of crystalline phases from solid gel precursors and the crystallization of zeolitic materials from solution under hydrothermal conditions. A wide range of studies that have been performed under nonambient conditions are discussed under the following headings: X-ray and neutron methods, spectroscopic and resonance methods, and imaging methods. Some current trends and future developments are assessed.

Introduction

Sol−gel reactions play a central role in the synthesis of many important classes of materials, including ceramics, polymers, and nanoporous solids such as aluminosilicate zeolites. As the importance of such reactions has grown, so too has the need to obtain a better understanding of their pathways, kinetics, and mechanisms. Considerable insight can, of course, be garnered from sampling a reaction at regular intervals and interrogating the samples ex situ by appropriate physical methods, but more detailed and reliable information can be obtained by performing in situ measurements. The purpose of this short review is to describe some of the techniques that have been used to perform such in situ studies and to examine the kinds of information that they yield. We are not aware of any previous reviews of this emerging field, but other authors have discussed the role of in situ methods in areas such as catalysis[1] and the study of aerosols.[2]

The chemistry of the liquid state is very important and often plays a crucial role in sol−gel synthesis. The sol−gel process involves the conversion of a solution of molecular precursors by a chemical reaction into a sol or a gel, which is subsequently transformed into a crystalline material upon drying, densification, or calcination. Precursor modification in the liquid has been recognized as an important aspect in sol−gel chemistry[3,4] and in the processing of ceramics,[5,6] including thin films.[7] The conditions under which hydrolysis and condensation of precursor species take place and the mechanism of growth and aggregation of colloidal particles are known to determine crystallization temperatures and reaction times. The environment of the cations and the identity of anions present in the liquid phase may play a determining role since they may control the structure and morphology of the final material, thereby opening up the possibility of material design. This in turn has been driving an interest in understanding the inner-shell modifications caused by chemical complexation in the liquid phase. In situ studies of such solution processes have not, however, been dealt with in any detail in this review, since they are performed under ambient conditions and do not present difficult technical challenges in terms of special environments or instrumentation.

In situ studies can yield a variety of different types of information. In some cases, they may shed light on the process of nucleation and the nature of the molecular species that are involved at this stage. In others, the emphasis may be on the energetics and kinetics of growth and the identity of any intermediate phases. We shall structure our discussion under three broad headings: (i) the use of X-rays and neutrons as probes, mainly in diffraction and small-angle scattering studies, (ii) the use of spectroscopic and resonance methods, and (iii) the use of imaging techniques, ranging from optical and electron microscopy to atomic force microscopy. We shall also highlight some of the combined approaches that are now being developed. Our discussion does not aim to be comprehensive but endeavors to be illustrative of the kinds of experiments that are now possible.

Examples will be taken from two general areas: (i) high-temperature studies of solid-to-solid conversions, such as the crystallization of a ceramic from an amorphous gel precursor and (ii) the crystallization of solids from aqueous sol−gel media, e.g., the formation of a zeolite under hydrothermal conditions in an autoclave. Solid-to-solid conversions are relatively easy to study by using techniques such as high-temperature X-ray powder diffraction, neutron powder diffraction, electron microscopy, X-ray absorption spectroscopy (especially EXAFS), nuclear magnetic resonance, and infrared spectroscopy, and the special environments that are required for such experiments are not particularly demanding. The tools that can be used to study crystallizations from solution include most of the above but also include probes that are specifically designed for studies of solutions or are not well suited to studying solid-to-solid conversions, e.g., small-angle X-ray and neutron scattering, light scattering, and optical microscopy. It is apparent that studies of crystallizations from solution often require more ingenuity in the design of

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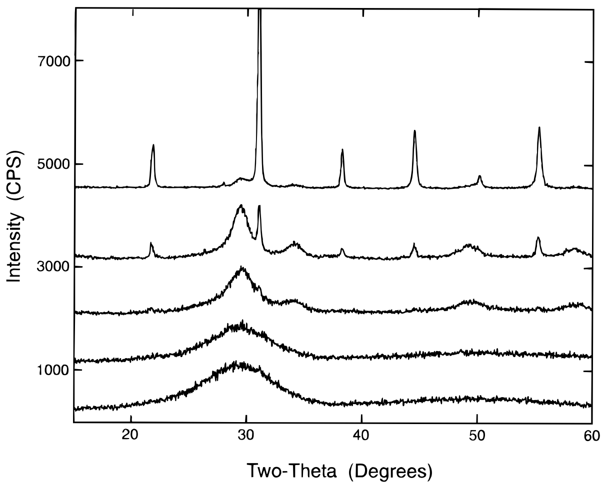

Figure 1. X-ray powder diffraction patterns of PZT samples collected during crystallization at (from bottom to top) 25, 350, 400, 450, and 500 °C. Broad peaks from the fluorite intermediate (seen at ~30, 33, and 49°) are clearly visible at 400 and 450 °C. Reproduced with kind permission from ref 9.

suitable in situ cells.

X-ray and Neutron Methods

Laboratory X-rays. In situ laboratory X-ray diffraction affords an inexpensive and convenient method for studying solid-state transformations such as gel crystallization and aging at high temperatures, since facile control of both temperature and atmosphere is possible. Different types of information pertaining to sol−gel transformations can be retrieved from diffraction measurements, including the kinetics of the digestion of an amorphous or crystalline phase, the crystallization of products, solid−solid transformations, and the evolution of the product crystallinity. In addition, there exists the possibility of probing the influence of synthesis parameters such as gel composition, templates, pH, temperature, and time. A further advantage of in situ X-ray techniques is that they provide an opportunity to observe the formation of precursors and intermediates, especially in the case of short-lived species that are structurally significant and stable at high temperatures.

The kinetics of the crystallization process are studied by following integrated intensities of selected reflections with time. Rate constants and reaction orders can be determined by fitting the growth of a selected reflection to the Avrami equation:[8]

$$\alpha = 1 - \exp(-kt^n)$$

where α is the extent of reaction, k is a rate constant, n is the order of the reaction, and t is the elapsed time. Activation energies for the crystallization process may be obtained by following the temperature dependence of the kinetics. The growth of the particle size during the crystallization can be monitored by measuring the full widths at half-maximum (fwhm) of selected reflections with time.

In a typical example of such as study, the crystallization of $PbZr_{1-x}Ti_xO_3$ [$x = 1$ (PT); $x = 0.55$ (PZT); $x = 0$ (PZ)] from alkoxide gels has been examined[9] while heating the sample from room temperature to 500 °C (Figure 1). Higher crystallization temperatures were observed in the sequence PT < PZ < PZT, with a change from first-order to second-order kinetics as the temperature was raised. In a series of constant temperature experiments, the leveling off of the fwhm's before the completion of the crystallization process (Figure 2) showed that the particle size converged to a limiting value during crystallization. Furthermore, the limiting value was shown to increase with temperature, indicating that the final particle size was dictated by the initial concentration of nucleation sites. The formation of a pyrochlore or fluorite-type intermediate was observed in the case of PZ and PZT (Figure 1); this is believed to reduce the driving force for the perovskite crystallization, therefore reducing the nuclei density and leading to a larger final grain size in these systems. Neutron powder diffraction studies on PZT are currently in progress at Lucas Heights in Sydney.[10]

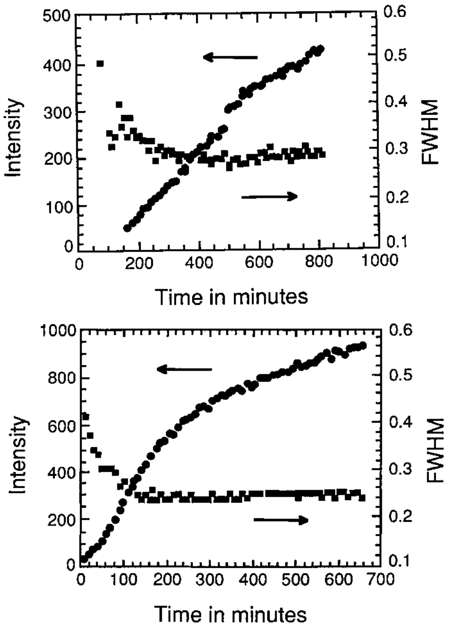

Figure 2. Growth of the integrated intensity of the (110) perovskite reflection (left-hand scale) and the full-width at half-maximum (right-hand scale) as a function of time for PZT at (upper) 480 °C and (lower) 500 °C. Reproduced with kind permission from ref 9.

Powder XRD has also been used to investigate the dynamics of zirconia synthesis from zirconium hydroxide solution.[11] In this case, the pH used in the preparation of the hydroxide was shown to affect the onset temperature and growth kinetics for both the crystallization and the solid−solid transformation from the tetragonal to the monoclinic phase.

Synchrotron X-rays. When compared to conventionally generated X-rays, the high brightness of synchrotron radiation makes it possible to measure large amounts of diffraction data in very short time periods or to collect high-resolution data in minutes rather than hours. In situ X-ray diffraction experiments on gels have been reported in both the energy dispersive diffraction (EDD) mode[12−19] and the monochromatic mode.[20−23] The EDD method harnesses the full spectrum of the polychromatic beam, since it uses the energy coordinate rather than the 2θ spatial coordinate to separate different reflections. Data can therefore be collected at a fixed diffraction angle with a small aperture, which is a significant advantage when access to the sample is restricted by a special environment.

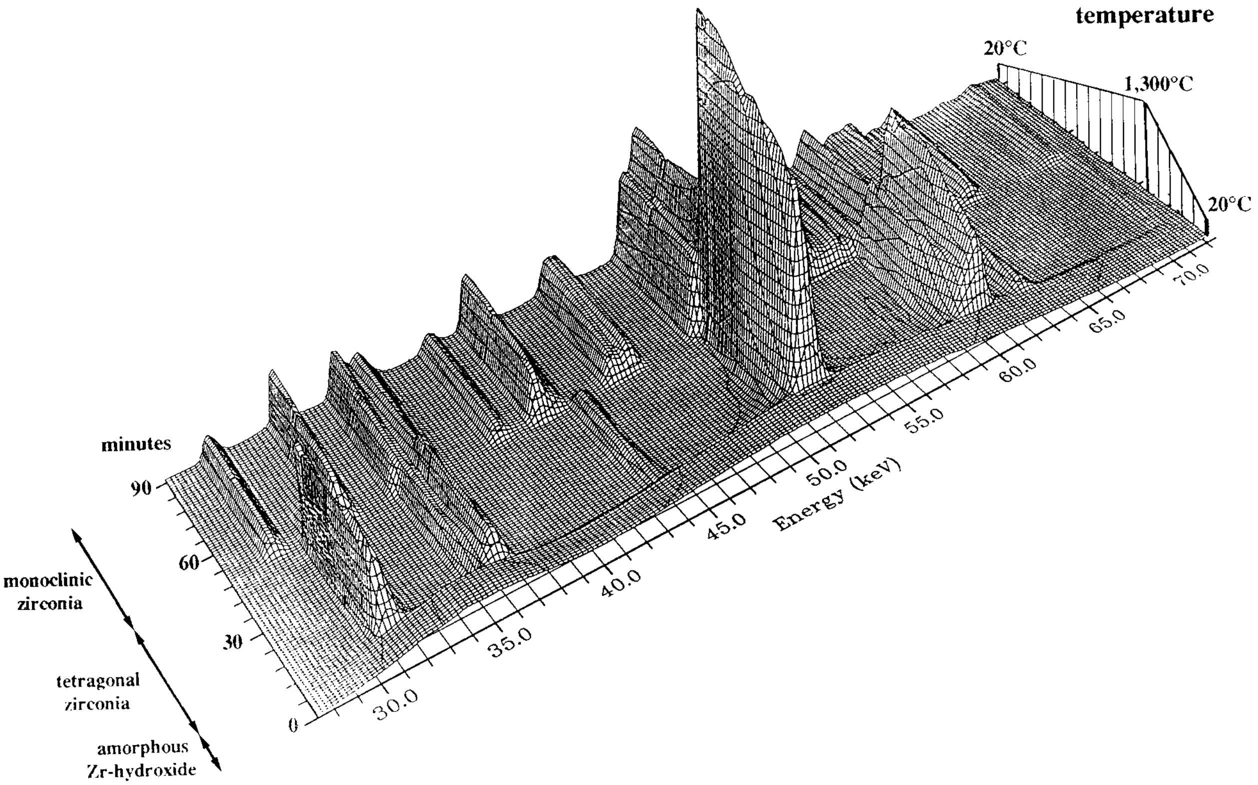

Figure 3. Synchrotron X-ray powder diffraction data, collected in the EDD mode, showing the crystallization of zirconia from an amorphous zirconium hydroxide precursor (see text for more details). Reproduced from ref 14 with kind permission from Elsevier Science—NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

Figure 3 shows an elegant example of an EDD study[14] in which an amorphous zirconia precursor crystallizes to form tetragonal zirconia on rapid heating and then transforms to the monoclinic form on cooling; note that all the data were collected in only 90 min. The advantages of using the EDD beam geometry are discussed in more detail in ref 12. The main disadvantage of the EDD method is the poor resolution; this stems from the low energy resolution of solid-state detectors and may be a serious limitation when studying low-symmetry structures with large numbers of overlapping Bragg peaks.

Environmental cells have been developed for studying in situ sol–gel crystallizations by EDD synchrotron methods. Figure 4 describes a typical set up at the Daresbury Laboratory,[12,13] suitable for either autoclave or open conditions, and heated by circulating water for temperatures up to 95 °C or silicone oil for higher temperatures. The inner surface of the cell is adapted to support corrosive alkaline solutions and to provide an inert environment for the synthesis; there is also the possibility of spinning the cell if preferred orientation or poor sampling effects cause problems. Using this apparatus, studies have been carried out on the hydrothermal synthesis of various materials, including the zeolites sodalite and A[13] and the aluminophosphate molecular sieve, VPI-5.[12]

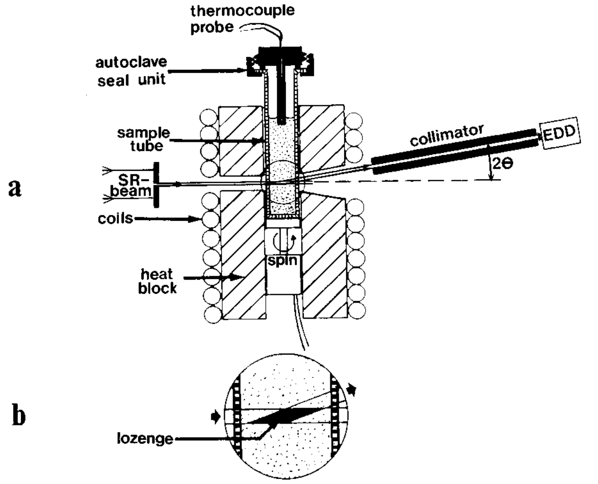

Figure 4. Schematic diagram (not to scale) illustrating the synchrotron radiation EDD geometry and the autoclave synthesis cell. The sample tube is typically 40–50 mm in length and 12 mm in diameter. Reproduced from ref 14 with kind permission from Elsevier Science—NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

Other in situ EDD studies have been reported using a "fixed-cell" geometry device.[15−19] For example, Rey et al.[17] studied the growth and stability of aluminophosphates (ALPOs) and their metal-substituted analogues (MeALPOs), the formation of which is known to be strongly dependent on the choice of the organic templates. The template-mediated formation of ALPO-5 and CoALPO-5 catalysts could be compared by tracking the dynamics of crystal growth from a mother liquor at 165 °C in the absence and presence of cobalt acetate, respectively. While both syntheses have similar induction periods of ~20 min, the formation of a chabazite-type intermediate was observed in the case of CoALPO-5.[17] More recently, investigations on the hydrothermal synthesis of the microporous oxofluorinated gallophosphate, ULM-5, highlighted the importance of the phosphorus source in the reaction pathway and the dynamics of crystal growth.[19] When orthophosphoric acid was used as the phosphorus source, ULM-5 forms rapidly after an initial induction period; when phosphorus pentoxide is used, a previously unobserved intermediate is formed, which subsequently reacts to form ULM-5. As illustrated above, in situ synchrotron radiation EDD methods are efficient in giving access to the complexity of the mechanisms taking place during hydrothermal synthesis and pinpointing the differences between various reactions procedures.

Although the use of the white X-ray beam emanating from the synchrotron is very attractive for in situ diffraction work, there has nevertheless been some effort in the direction of using monochromatic techniques.[20−23] The advantages of constant-wavelength methods are (i) the resolution is better; (ii) very short wavelength X-rays, which are more penetrating, can be used (this will become more important with the third-generation synchrotron sources and obviously has attractions for studies in special environments); (iii) one can take advantage of resonant diffraction effects at absorption edges. Constant-wavelength in situ synchrotron powder diffraction studies have been made on a Huber diffractometer at the beam line X7B at NSLS, Brookhaven National Laboratory. In a study on MeALPOs (magnesium aluminophosphate),[20b] the details of the influence of the templates on the final products were explored. In these cases, the samples were kept in 0.5−0.7 mm diameter quartz capillaries at an internal pressure of up to 45 atm and heated in hot air; an image plate area detector was used to record the powder patterns.

Another recent study on the same instrument describes the use of synchrotron radiation at constant wavelength for studying the kinetics of the formation of single crystals of the clathrasil, Dodecasil-3C (Figure 5).[22] The formation of a small number of single crystals, rather than a powder, was serendipitous, but the work points to the possibility of elucidating crystallization mechanisms by single-crystal methods and capturing phenomena occurring in the course of single-crystal growth (such as chemical composition variations, changes in framework Si/Al ordering, the formation of defects, etc.).

Small-Angle X-ray Scattering (SAXS). The above paragraphs illustrate the power of X-ray diffraction methods for the study of crystallization processes from sols and gels, but they also remind us that diffraction methods are intrinsically insensitive to the structures of the nuclei that are formed during the induction period because the length scales of such nuclei are too small to be observed by XRD. To study nucleation processes, therefore, the use of techniques that probe shorter length scales, such as small-angle X-ray and neutron-scattering methods (SAXS and SANS), are of special interest. In practice most of the small-angle scattering work in the area of sol−gel synthesis has utilized neutrons rather than X-rays. The discussion of this area will therefore be found in the neutron section, below.

X-ray Absorption Spectroscopy (XAS, EXAFS). X-ray absorption spectroscopy techniques, especially EXAFS, also hold promise for studying in situ processes. These experiments are easy to perform, especially with the new synchrotron radiation sources that provide a broad-band, tunable source of radiation with uniform intensity in the X-ray region. Because absorption edges of different elements are well separated, it is possible to look selectively at a specific chemical constituent of the system, even when present in high dilution, and to probe its site environment in terms of bond distances and coordination number. EXAFS techniques are especially suited for systems where no long-range order exists, such as structurally disordered or amorphous media occurring prior to a crystallization process.

The advantages of in situ EXAFS were first recognized in the field of heterogeneous catalysis, where it has been used to quantitatively probe the environment of an active site at a solid surface.[1] In the context of sol−gel synthesis, Landron et al.[24] have developed an appropriate cell for in situ EXAFS measurements at the synchrotron facility, LURE (Orsay). They have reported data relating to zirconia aerosol precursors and compared them to the EXAFS spectra of monoclinic zirconia and zirconium nitrate hydrate. In contrast with monoclinic zirconia, they find that the environment of zirconium atoms in the nebulized solution is similar to that of the powder of zirconyl nitrate hydrate (four OH groups, two H_2O molecules, and two oxygens atoms of the ligand). Interestingly, these results demonstrate that the identity of the complexes present in the nitrate solution during zirconia synthesis is maintained during the drying of the precursor, unlike the high-temperature transformation leading to the monoclinic structure.

In conjunction with X-ray diffraction, EXAFS offers an even more complete picture of the system, yielding a time-resolved tracking of local structure formation during the long-range ordering process associated with the crystallization. This combined approach is particularly attractive for following the evolution of the local site environment of a selected element as a system undergoes nucleation and crystallization. Such investigations have been driven by the development of dedicated instrumentation (Figure 6) for the study of heterogeneous catalysis at the Daresbury synchrotron radiation source.[25] By using a photodiode array for recording the X-ray absorption signal and a position-sensitive detector for the X-ray diffraction data, it has proved possible to follow changes in both the short-range and the long-range crystallographic order during the synthesis of an active metal catalyst from its powder compound precursor. More recently, the same group has studied the structural and kinetic evolution of a stuffed quartz phase from the amorphous product of the decomposition of Mg−B zeolite, and the subsequent formation of cordierite at 1000 °C.[26] When adding traces of pure ZnO to the synthesis, the incorporation of Zn^{2+} into the aluminosilicate structure is shown to induce the collapse of the zeolite structure and to accelerate the formation of cordierite, finally leading to a crystallization temperature that is 100 °C lower than in the absence of ZnO. As will be discussed later in more detail, combined techniques always yield more information than individual techniques.

Neutrons. An important advantage of using neutrons rather than X-rays for in situ studies is that neutrons have low absorption cross sections, a property that makes them especially suited for studying materials in special environments such as cryostats, pressure cells, and autoclaves.[27] Other advantages of neutron diffraction are that they can probe light atoms, e.g., hydrogen, that are poor X-ray scatterers, and that there is a dramatic difference between the scattering powers of hydrogen and deuterium, allowing the development

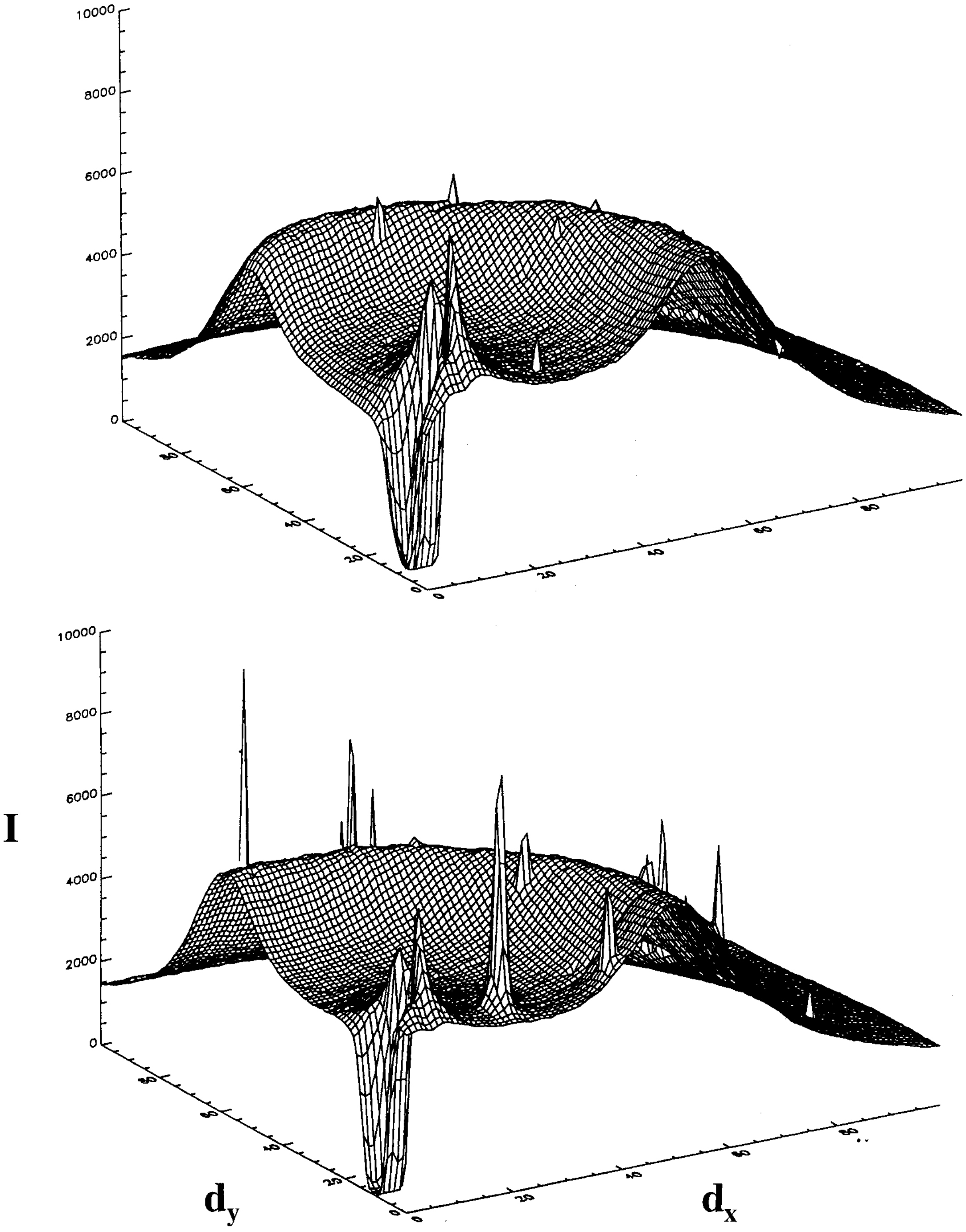

Figure 5. Single-crystal X-ray reflections of dodecasil-3C, evolving under in situ conditions at 180 °C (upper, 30 min; lower, 165 min). The X-ray intensity (I) is plotted on the vertical axis, and distances (d_x, d_y) on the image plate from the incident beam path are plotted on the horizontal axes. The broad annulus of scattering arises from both the gel precursor and the quartz capillary. Adapted from data given in ref 22.

of contrast matching methods that are discussed later. A particular advantage of neutron diffractometry is that the large incoherent scattering cross section of hydrogen gives rise to very high backgrounds in diffraction patterns, the evolution of which may be used for monitoring the loss of hydrogen-containing species, e.g., organics, from the sample (see below). On the other hand, the low fluxes associated with neutron sources restrict their applications to processes taking place over hours rather than seconds.

In situ neutron powder diffractometry was pioneered at ILL (Grenoble) by Pannetier and co-workers[28] and applied extensively to the study of solid−solid transformations in a variety of inorganic reactions, e.g., dehydrations, decompositions, phase transitions, intercalation, etc. In the area of sol−gel synthesis, neutron powder diffractometry has been exploited for studying the hydrothermal synthesis of basic zeolites and of a layered calcium silicate hydrate[29] and more recently for investigating the crystallization of zirconia from zirconium hydroxides.[14,30] Figure 7 shows the time/temperature-resolved neutron-scattering patterns observed for zirconium hydroxides, prepared at high pH. The first loss of incoherent hydrogen scattering above 150 °C is attributed to the removal of loosely bound water molecules from the gel, while the second abrupt loss at 490 °C is attributed to a delayed and cooperative oxolation

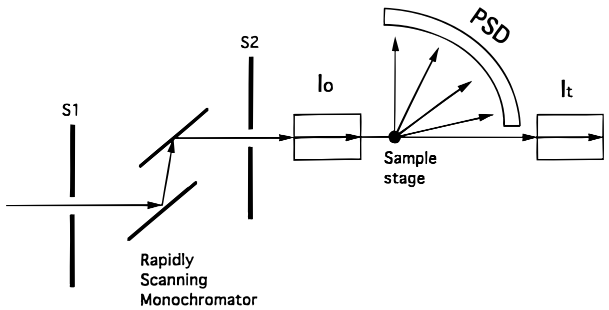

Figure 6. Experimental arrangement for a combined EXAFS/XRD experiment. S1 and S2 are monochromator entrance and exit slits to define the energy resolution and limit the background scatter, respectively. I_0 and I_t are the reference and transmission ion chambers, respectively, used to record the EXAFS spectra. PSD represents the curved position-sensitive detector that records the XRD patterns. Reproduced with kind permission from ref 26.

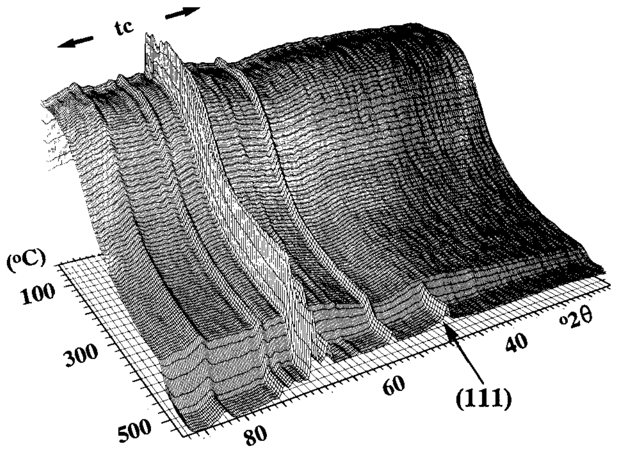

Figure 7. Time/temperature-resolved neutron diffraction patterns showing the calcination of zirconium hydroxides prepared at pH = 10.35. Around 490 °C, there is a dramatic reduction of background just before the first appearance of the (111) tetragonal zirconia peak. The permanent peaks (tc) are due to the thermocouple assembly. Reproduced from ref 14 with kind permission from Elsevier Science − NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.

process from which rapid crystallization of zirconia can proceed.

Small-Angle Scattering Methods. Valuable insight into the nature of gels and crystallite nucleation may also be achieved by small-angle scattering methods. There are now good examples of the use of small-angle X-ray and neutron scattering, often in a combined way, investigating the crystallization of ceramics[31] or zeolites[32−36] from solutions. The theory for treating SANS and SAXS in terms of aggregates of spherical particles is well developed and can be used for determining the radius of the spheres, the fractal dimension, and the size of the aggregates.[37]

The intensity of the small-angle scattering from a homogeneous solid gel particle suspended in a liquid depends on the difference in scattering length density between the solid and the liquid phases. The advantage of neutron scattering over X-ray scattering is that it is possible to use isotopic substitution, especially with hydrogen and deuterium, so as to modify the contrast between the scattering length densities of the particles and the solvent. These isotopic contrast matching methods allow one to determine the chemical composition of the particles in the mother liquor. Such approaches have already proved to be efficient for investigating the crystallization and aging processes during the template-mediated synthesis of ZSM-5 and silicalite.[32−34] The important difference between the scattering factors of hydrogen and deuterium is exploited either by labeling the tetrapropylammonium (TPA) ion or by varying the D_2O/H_2O ratio of the mother liquor (or both). In this way, contrast match between the particles and the solvent may be reached, thereby differentiating between pure silicate particles and those containing the organic template within the ZSM-5 nuclei. SANS measurements can therefore be conveniently used for monitoring the incorporation of the template into the scattering particles.

A combination of both SAXS and contrast-matched SANS was used for investigating the room-temperature aging and crystallization of ZSM-5[32,33] and silicalite[34] in the above work. During the aging period, which can be defined as the time elapsed between the mixing of reagents and the onset of heating to the reaction temperature, the growth of particles in the 1−10 nm size domain was observed during the first 60 h.[33] An estimation of the amount of silica contained in the scattering particles showed that the cessation of growth is due to the formation of an equilibrium state rather than to the consumption of all reactive species. The lack of an aging process in the absence of aluminum was demonstrated by comparing SAXS data from solutions with and without aluminum present, suggesting that aluminum drives the gelation process as a cross-linking agent between larger silicate species, giving rise to a loosely linked network of aluminosilicate species. The contrast matched SANS measurements showed that the particles formed in room-temperature aged solutions had the same contrast as the template-free silica gels, therefore showing that the particles formed during the aging process are not deemed to be template-containing crystal nuclei. Interestingly, by performing similar combined SAXS/SANS measurements during the high-temperature crystallization process,[34] the same group monitored the transformations occurring during the induction period for the template-mediated synthesis of silicalite from a clear nongelling solution heated at 100 °C. SANS measurements detected the template-induced growth of particles about 200 Å in size and with a composition close to that of silicalite, therefore suggesting they may be nuclei for the macroscopic silicalite crystals. This kind of study opens the field for investigations of the temperature dependence of the early stages of the crystallization process in terms of kinetic and thermodynamic features.

In the area of ceramics, in situ SANS measurements have been performed using a new high-temperature furnace designed for monitoring ceramic processing.[31] The apparatus enables the study of the processing of materials at temperatures up to 2000 °C in an oxidizing, reducing, or neutral environment. Representative data were reported on the sintering behavior of a silica gel through the measurement of microstructural parameters such as the pore sizes, pore volumes, and pore surface areas.

Spectroscopic and Resonance Methods

Nuclear Magnetic Resonance (NMR). NMR is widely used to probe species in both the liquid and the solid states, and in situ methods are well developed for certain types of experiments. For example, extensive use has been made of NMR to study catalytic reactions in situ, and the area of acid-catalyzed reactions has been reviewed by Haw et al.[38] Such processes may involve measurements at low or high temperatures, and they can be studied by static methods (when the species involved are highly mobile under reaction conditions) or by the use of magic angle spinning, MAS NMR (when the species of interest are immobile in the solid state). In the case of high-temperature MAS NMR, there have been a number of interesting studies that are pertinent to sol–gel reactions. For example, the structural phase transitions of tridymite have been studied at temperatures up to 400 °C by MAS NMR,[39] and the formation of glasses from silica melts has been examined at temperatures as high as 600 °C.[40] Of course, NMR is particularly well suited to the study of silicate minerals and related materials because they typically contain a number of good NMR nuclei, e.g., ^{27}Al, ^{29}Si, ^{31}P, ^{1}H, ^{13}C, ^{15}N.

As was discussed in an earlier section, the synthesis of a zeolite is normally carried out in a stainless steel autoclave under hydrothermal conditions in the temperature range 100–200 °C. Aging of the sol or gel, prior to reaction, is often important. The study of the silicate species that are present in the initial gel, prior to heating, is straightforward by NMR and has been described by several groups;[41–44] ab initio quantum mechanical calculations of NMR shifts have proved to be useful in the assignment of the different resonances to particular silicate species.[45] The largest species that has been identified in such studies is the double-four ring, and characterization of the silicate moieties that are present as further condensation takes place, i.e., during the nucleation of the zeolite, has proved elusive. It has, however, been possible to use ex situ 2-D NMR methods to demonstrate that an organic template molecule is associated with the silicate nuclei during the nucleation process.[46]

In relation to crystallizations from solution, there are several in situ studies of particular interest. Brough et al. have studied the polymerization of silicate species in model cement systems by in situ MAS NMR.[47] Measurements were performed on samples enriched with ^{29}Si because of the relatively poor signal that was obtained from such complex samples with natural-abundance ^{29}Si. In this example, the equilibration and data collection were performed at room temperature, so no special experimental problems needed to be addressed. Higher temperature condensation reactions of aluminate species have recently been examined under autoclave conditions in the temperature range up to 130 °C; a thick Pyrex NMR tube, closed by a Teflon valve, was used to contain the sample.[48] Excellent spectra were obtained, albeit under static rather than spinning conditions. In the zeolite area, however, Shi et al. constructed a simple rotor in which a liquid sample could be sealed and held at high temperatures during magic angle spinning.[49] Both ^{27}Al and ^{29}Si spectra were collected during the synthesis of sodium zeolite-A at 65 °C (Figures 8 and 9); note that the ^{29}Si spectra have poorer statistics arising from the lower sensitivity compared to ^{27}Al. Prior to reaction, the ^{29}Si spectrum is dominated by isolated silicate monomers (approximately −72 ppm) and a broad resonance (approximately −75 to −95 ppm) from the gel. Corresponding features are seen in the ^{27}Al spectra. During the induction and nucleation period, which lasts about 40 min, both the silicon and aluminum spectra remain unchanged, indicating, unfortunately, that MAS NMR is insensitive to these events. During the growth period, however, the NMR lines narrow as long-range order is established, and the results correlate very nicely with the findings from X-ray diffraction.

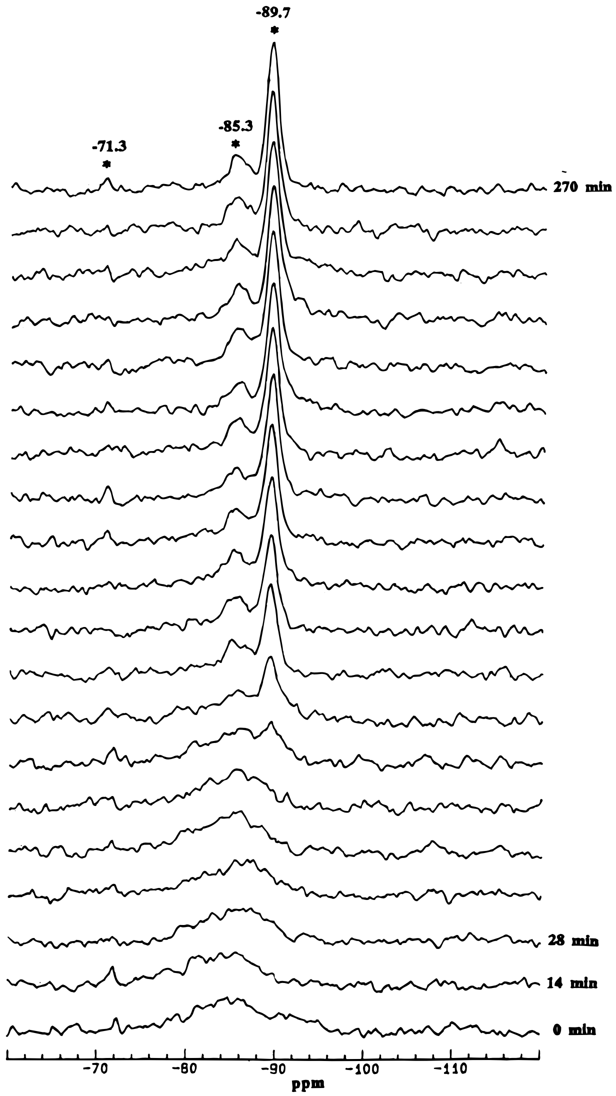

Figure 8. In situ ^{29}Si MAS NMR spectra of a zeolite A synthesis from a gel at 65 °C. Spectra were collected at intervals of approximately 14 min (after 30 min of mixing). Reproduced with kind permission from ref 49.

Excitement arising from the recent discovery[50] of the so-called mesoporous molecular sieves (i.e., the MCM-41 family of materials) has also stimulated in situ NMR studies on the formation of and interconversions between these materials. Since these materials are synthesized in the presence of surfactant molecules that are incorporated into the final product, the self-assembly of the surfactant array and the condensation of the silicate matrix may conveniently be studied by monitoring the dynamics of the surfactant side chains using ^{2}H NMR.[51] The different phases (e.g., lamellar, hexagonal, and cubic) can readily be identified by ^{2}H NMR from the characteristic splittings of their Pake doublets, and their interconversions, which are reversible under cer-

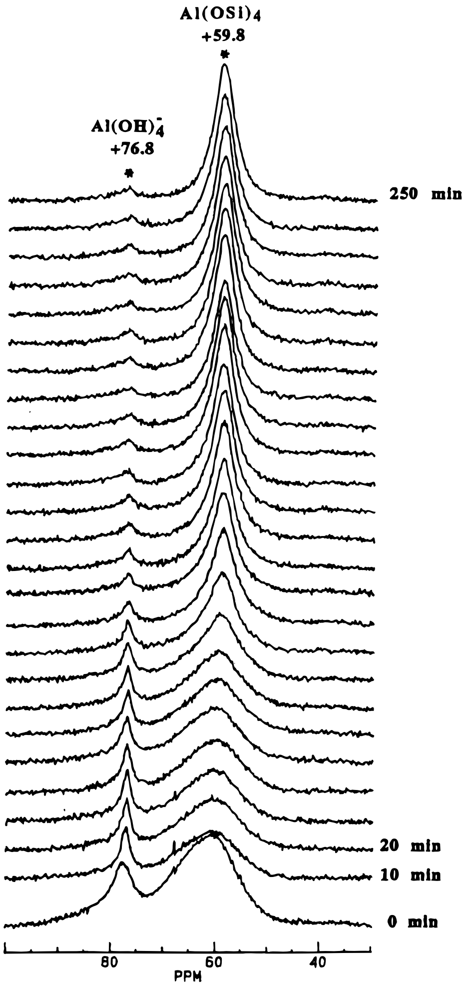

Figure 9. In situ ^{27}Al MAS NMR spectra of a zeolite A synthesis from a gel at 65 °C. Spectra were collected at intervals of approximately 14 min (after 30 min of mixing). Reproduced with kind permission from ref 49.

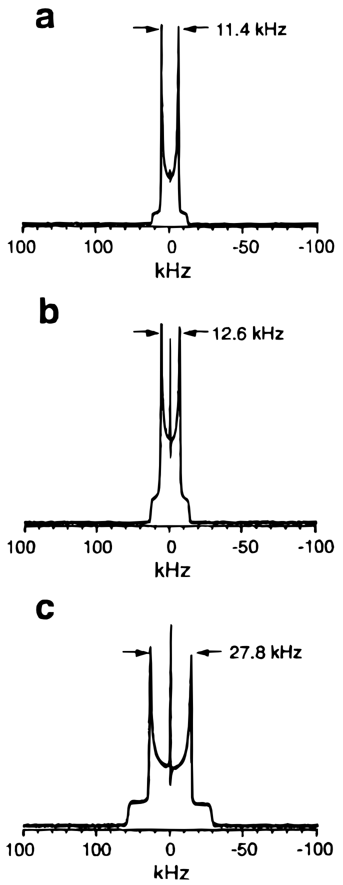

Figure 10. In situ ^{2}H NMR showing (a) the spectrum from the CTAB surfactant precursor, (b) that of an hexagonal silicate-surfactant liquid crystal, and (c) the spectrum of a lamellar silicate–surfactant liquid crystal. The surfactant molecules were selectively deuterated at the α-carbon position. Reproduced with kind permission from ref 51.

tain conditions, have been followed in situ (Figure 10). Such interconversions have also been followed at room temperature by X-ray powder diffraction.[52]

Vibrational Spectroscopy. In common with NMR, vibrational spectroscopy methods, which include infrared and Raman spectroscopy, afford convenient probes of local rather than long-range structure. They certainly lend themselves to in situ approaches and have been widely used for studies in areas such as heterogeneous oxidation catalysis,[53,54] electrochemistry,[55] surface science,[56] and polymer chemistry.[57] Applications in the sol–gel area are rather few, especially in the context of synthesis, but the examples below provide a measure of the scope in this area.

As with other techniques, the application of in situ methods to solid-to-solid transformations is relatively straightforward, and there have been several applications of this type.[58,59] In the case of Raman spectroscopy, the work by Lu and Schrader[58] on the crystallization of sol–gel derived Ba–Ti–O thin films provides a typical example. Dielectric materials such as the barium titanates are poor Raman scatterers, but developments in detector technology, together with the judicious choice of substrates, makes possible the rapid collection of data, in situ, even from thin films. In this particular instance, the crystallization of $BaTi_5O_{11}$ was monitored on a Si/Pt substrate during isothermal annealing at 770 °C over a 90 min period; data were collected every 10 min. The intensities of selected peaks in the Raman spectra were monitored as a function of time, and the data were fitted to the Avrami equation. The findings from such studies are very similar to those obtained from powder diffraction experiments (see section on X-ray and Neutron Methods), shedding light on the growth kinetics but yielding very little information concerning the nucleation process.

The use of Raman spectroscopy to study crystallizations from solution has been limited to measurements on gels that have been separated from the solution phase by centrifugation (solutions can be studied by Raman spectroscopy, but scattering effects preclude observations from typical sols or gels). Twu et al.[60] examined the kinetics and mechanism of the synthesis of faujasite zeolites from two different sources, Ludox and N-brand. The gel samples contained both solid and liquid phases, and the Raman spectra provided information concerning silicate, aluminate and aluminosilicate species in solution, as well as the formation of the crystalline zeolite framework (which gives rise to a characteristic framework band at ~500 cm^{-1}). Interestingly, it was found that the Raman spectra were sensitive to the crystallization of the zeolite well before it became apparent in the X-ray diffraction patterns. Although the work of Twu et al. was performed ex situ, these studies underline the strengths of the Raman technique and the considerable scope for in situ work

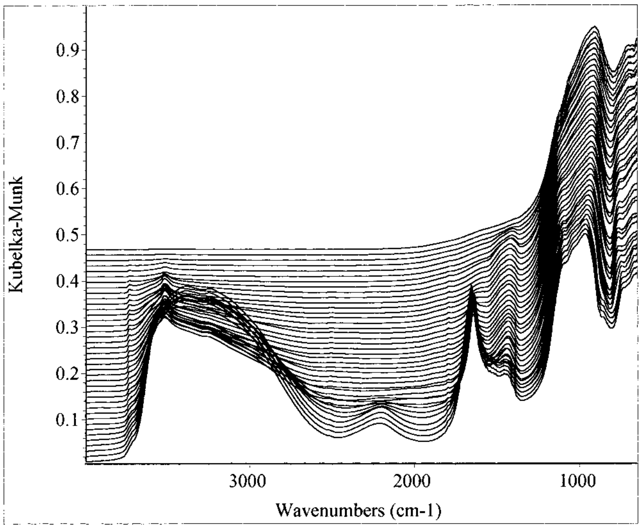

Figure 11. In situ DRIFTS spectra showing the loss of the hydroxyl and water bands during the dehydration of zeolite Ca-MAP as a function of temperature in the range 30−550 °C. Unpublished results.[62]

on the crystallization of silicates and related materials.

There has been even less work on sol−gel synthesis by in situ infrared spectroscopy, although the procedures for such studies are well-established from work in other areas. In situ IR methods are routine, for example, in catalysis, electrochemistry, chemical vapor deposition, and interface chemistry. Recent work[61] on the formation of hybrid organic/inorganic composites from sol−gel reactions of siloxanes in polymeric media, however, has given considerable insight into the condensation reactions that take place during this process, thus emphasizing the scope for more work of this type. Solid-to-solid studies are relatively easy to carry out, e.g., by diffuse reflectance IR spectroscopy, as is illustrated by the high-temperature work on the dehydration of sodium zeolite MAP (Figure 11).[62] One recent development that augurs well for in situ IR studies under more difficult reaction conditions is the development of real time monitoring systems using fiber optics for the transmission line that carries the IR to and from the reactor.[63] This is more practicable using near IR (NIR) spectroscopy (14 000 to 4000 cm^{-1}), rather than conventional (mid) IR spectroscopy (4000−400 cm^{-1}), since the NIR frequency range can be transmitted with a conventional silica-based optical fiber.

Other Spectroscopic and Resonance Methods. A wide range of other spectroscopic methods have been used for in situ studies of sol−gel synthesis. For example, electron paramagnetic resonance (EPR) is a powerful and sensitive probe for paramagnetic systems. Although most of the inorganic materials that are prepared by sol−gel routes are diamagnetic, EPR is very useful for some interesting organic polymer and hybrid organic/inorganic systems. In a recent study, a paramagnetic nitroxide free radical (4-oxo-Tempo) was used to probe the structural and chemical changes taking place during sol−gel glass formation with silica.[64] The spectral changes, which were monitored at room temperature, reflect variations in the composition, the effective viscosity, and the polarity of the cage media in the vicinity of the probe. Paramagnetic probes are also sensitive to short-lived free radicals that may be created during hydrolysis and polycondensation.

Other spectroscopic techniques that have been used, in situ, include fluorescence spectroscopy (e.g., by incorporating a fluorescent probe into a reaction)[65] and ion-beam analysis.[66] In the case of the ion-beam study,[66] the densification of a sol−gel zirconia thin film was induced by bombardment with inert gas (Ar, Ne, Kr) ions, rather than by heating, and the resultant changes were monitored in situ by ion backscattering measurements (He) in the same instrument. Thin-film processing can also be monitored by spectroscopic ellipsometry, and some interesting in situ work has been carried out on the growth of PZT films from sol−gel precursors on sapphire and Pt-coated silicon substrates.[67] Such studies can probe the loss of organics due to pyrolysis and the evolution of film thickness, roughness, and optical properties with time and temperature.

Imaging and Optical Methods

Optical Microscopy and Light Scattering. The direct observation of crystal growth from solution can provide useful information relating to the kinetics of crystallization, the activation energy for growth, and the evolution of crystal morphology. A number of papers have dealt with the in situ observation of zeolite crystal growth by optical microscopy.[68,69] Recently, Iwasaki et al.[70] developed two optical microscopy strategies for monitoring the growth of individual zeolite crystals, in situ, from solution: one for clear solutions and the other for gels. Results were obtained for zeolites ZSM-5 and silicalite, grown during steaming at ~170 °C. The disadvantage of optical microscopy is that the resolution is limited by the wavelength of the radiation, so that even under ideal conditions the spatial resolution cannot be better than ~2000 Å. In the work of Iwasaki et al., for example, the initial observations were made when the crystals were ~1 μm. Nevertheless, such studies afford unique insight into the influence of growth parameters on the evolution of crystal morphology.

In contrast to optical microscopy, light scattering provides information about crystal growth at an earlier stage of the crystallization; since it is not an imaging method in the technical sense, the resolution is not wavelength-limited. The scattered intensity is proportional to d^6, where d is the diameter of the scattering particle, so the problem with small particles is one of detectability rather than resolution. In a recent in situ study of the initial stages of crystallization of the zeolite silicalite in the presence of TPA,[71] subcolloidal particles of diameter 3.3 nm were detected by using a high-effect laser light source operating at 514.5 nm (the scattered intensity is also enhanced by using shorter wavelengths since it depends upon λ^{-4}). These subcolloidal particles were present throughout the crystallization and remained essentially unchanged in size, but they coexisted with a second population of larger crystallites that were detected after approximately 9.5 h at ~70 °C; this second population, which corresponds to the growing silicalite crystals, was monitored as the size increased from ~12 to 25 nm. Evidence was presented to show that some of the subcolloidal particles may be zeolite nuclei.

Electron Microscopy. Electron microscopy offers much greater spatial resolution than light microscopy, but it is difficult to perform in situ experiments because electron−matter interactions are ~10^4 times stronger than those of X-rays, making it difficult to penetrate special environments. Furthermore, the electron microscope column has to be held under a good vacuum, thereby creating further obstacles. Nevertheless, some interesting work has been performed in the catalysis area.[72] As far as sol−gel synthesis is concerned, the study of crystallizations from solution would seem to be out of reach, given the experimental obstacles, but solid-to-solid transformations, such as gel crystallizations at high temperatures, are clearly feasible. The attraction of electron microscopy is that it can offer a wide range of experimental probes in addition to imaging, such as selected area electron diffraction, X-ray emission analysis (EDAX), energy loss spectroscopy (EELS), and so on.

A recent high-temperature transmission electron microscopy (TEM) study of the crystallization of barium titanate thin films at temperatures up to ~800 °C provides a nice example of such work.[73] Evidence was found to indicate that the amorphous gel films initially crystallized at ~600 °C as an intermediate oxocarbonate phase, with a particle size in the range 5−10 nm. Fine grains of $BaTiO_3$ then nucleated by the decomposition of this intermediate phase; the large weight loss associated with this transformation appeared to contribute to the residual porosity of the films. In addition to studies of barium titanate formation on (100) Si, comparative studies were carried out on MBE-grown $BaTiO_3$. All high-temperature TEM measurements were performed under the normal vacuum atmosphere of the electron microscope, though ex situ studies in air revealed strikingly similar results. In other chemical systems, the convenience of this simple approach may be less justifiable, and the use of differential pumping and a special in situ chamber may be necessary.[72]

Atomic Force Microscopy. In contrast to electron microscopy, atomic force microscopy (AFM) and related methods[74] can offer high spatial resolution under a wide range of experimental conditions. There has been a limited amount of ex situ high-resolution work on the morphology of zeolite single crystals,[75−78] but no in situ studies of their growth. The feasibility of such work is illustrated by some impressive real-time studies of the growth (and dissolution) of calcium carbonate crystals in aqueous solution at room temperature;[79,80] such experiments take advantage of the development of tapping mode AFM,[81] which facilitates the measurement of images from samples under liquids. The extension of such work to crystallization processes under hydrothermal autoclave conditions remains a technical challenge, but one that is surely to be met soon.

Concluding Remarks

A brief glance at the list of references attached to this review reveals the high level of current interest in in situ studies of sol−gel synthetic reactions. The tools that are already available in this area represent an extraordinarily powerful portfolio, spanning methods for looking at local structure (e.g., EXAFS and NMR), techniques that probe long-range order (e.g., XRD and neutron diffraction), tools that examine the evolution of particle size or thickness with, say, time (e.g., SAXS, SANS and ellipsometry), and an extensive range of imaging capabilities (e.g., AFM, TEM, SEM, and light microscopy). As a result, in situ studies are now yielding a detailed understanding of the kinetics, pathways, and mechanisms by which sol−gel reactions proceed, and this in turn should lead to an improvement in our ability to control such reactions and to produce optimized, high-performance materials.

An important trend that has become apparent is the development of multitechnique approaches to in situ studies. Elegant examples include the combined SAXS/WAXS studies on silicalite crystallization[36] and simultaneous EXAFS/XRD measurements on cordierite formation from a zeolite precursor.[26] The future will inevitably see a trend toward higher sensitivity, higher resolution, and shorter time scales, these being driven by advances in both instrumentation and data analysis methods. For example, the recent commissioning of a new diffractometer, D20, at the Laue-Langevin Institute in Grenoble, will dramatically reduce the time needed to collect powder neutron diffraction data. Third-generation synchrotron sources (e.g., the Advanced Photon Source at Argonne and the European Synchrotron Radiation Facility in Grenoble), with their higher brightness, especially at the more penetrating, short X-ray wavelengths, will also provide exciting opportunities, as will a new generation of pulsed neutron sources. NMR will benefit from access to higher magnetic fields, which give greater sensitivity and better spectral resolution, and the development of more sophisticated pulse sequences ancillary equipment for wide-bore magnets. But perhaps the most eye-catching advances will be in the area of atomic force microscopy and related methods, where the possibilities are only just beginning to emerge.

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