

Final report of grant GR/L28647

Development of an Advanced Characterisation Methodology for Gel-Produced Materials

1. Introduction

This grant was aimed at improving understanding of, and models for, structural development in amorphous sol-gel produced materials as the gel turns eventually into a dense solid after calcination. Of central importance was the need to better understand better the preparation-structure-properties relations in such materials. The focus of this work was the addition of metals such as Ti and Zr to SiO_2 because of their technological potentialities. The materials' properties intimately depend on the structural role and distribution of the ions added. In multicomponent oxide systems not only can the structure change on the atomic scale but additional processes such as phase separation can alter the mesoscopic structure, both of which will effect the properties of the product. One of the most demanding current challenges for materials characterisation is to follow such processes simultaneously on their different length scales in amorphous solids, particularly the transition gel \rightarrow porous glass \rightarrow dense glass. Central to the approach adopted here was the application of an advanced characterisation methodology comprising diffraction (both X-ray and neutron), X-ray absorption techniques (EXAFS) and solid state NMR. It was essential to apply all these techniques to *identical* samples to build up extensive data sets that could be linked together to provide more complete structural insight. One of the main technical aims was transfer this information by into better calibration of "benchtop" IR data. Hence throughout this project IR data was recorded on the same samples from which that the other characterisation was reported. The significant interest in the literature in titania-doped silica for catalytic applications led to detailed examination of the modification of the reaction scheme to maximise the level of titanium that can be homogeneously distributed into a silica matrix, and the effect of tailoring the specific surface area (pore size) on the atomic scale structure.

As the project progressed it was clear that two key additions to the original project methodology would considerably improve the structural information available. First, X-ray near edge spectroscopy (XANES) offered complementary coordination information, especially for titanium. Second, the speed of techniques improved, particularly for X-ray methods, through more sensitive detectors and higher flux (e.g. at the ESRF). Both these aspects increased considerably the feasibility of *in situ* (even possibly real time) studies on bulk materials. This meant that the original objectives 1-4 were focused on and have essentially been fully met. To increase the technological applicability of the work a collaboration was started with Dr S.C.E. Tsang of the Catalysis Research Centre at the University of Reading to investigate the relation of the structural details to and catalytic properties of the materials.

2. Main Achievements

1. Obtaining the most extensive experimental data sets on the *same* samples of $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ ^{2,3,5,13,14} and $(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$ ^{1,4,7,9}. The data combined X-ray and neutron diffraction, EXAFS, XANES, ^{29}Si and ^{17}O magic angle spinning (MAS) NMR, FTIR and SAXS. This allowed the most unambiguous picture to date of the structure of these amorphous materials to be developed. This work showed the dangers of building structural models of such amorphous materials on limited data sets since in the literature this has led to incorrect model structures being suggested. Also, at all times the correlation of the detailed structural models with FTIR data on the same samples will greatly aid interpretation of IR data from such systems.

2. Reporting the first detailed structural study of sol-gel produced $(\text{Ta}_2\text{O}_5)_{0.5x}(\text{SiO}_2)_{1-x}$.¹⁰

3. Technique Development

3.1 Application of ^{17}O to show distinct Si-O-Ti linkages within the initial amorphous solid.^{1,2,6} The ^{17}O intensities were used to infer the degree of atomic scale mixing and to detect phase separation as samples were heated.

3.2 Calibration of XANES to show three distinct titanium sites in $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ xerogels, viz. TiO_4 , phase separated TiO_6 and isolated TiO_6 . The isolated TiO_6 rapidly change coordination on heating, but is reversible although the degree of reversibility is a function of time at the elevated temperature.^{3,5}

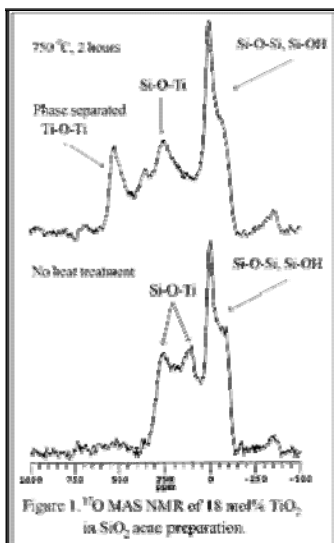
3.3 *In situ* studies at elevated temperature have been carried out for the gels using quick EXAFS and through the development of X-ray diffraction using a curved image plate. This is one of the first *in situ* diffraction studies using the weaker diffuse scattering of an amorphous system (as opposed to the sharp Bragg peaks associated with polycrystalline systems) where the method has been used to follow structural changes.^{8,13}

4. Materials Developments

4.1 Complexing the titanium precursor with acetylacetonate (acac) promotes Ti-O-Si bonding. On heating phase separation of TiO_2 occurs, but for samples initially complexed by acac the amount of Ti-O-Si bonding that persists at 750°C is increased.² The concentration limit of TiO_2 in SiO_2 at 750°C for sol-gel prepared sample is 10-15 mol%.

4.2 For $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ solvent exchange by heptane followed by slow drying has produced samples with a well defined, robust pore structure with high surface area, good atomic mixing and good catalytic activity.¹²

3. Scientific Aspects



3.1. Technique Development

NMR

^{29}Si MAS is a standard characterisation technique and much data has previously been reported from TiO_2 and ZrO_2 in SiO_2 but there has always existed some ambiguity as to the structural identity of the different ^{29}Si resonances observed. In this study, through correlation with ^{17}O NMR and the structural state of the titanium deduced from X-ray absorption methods, there is no doubt that the isotropic chemical shift differences of ^{29}Si are too small to distinguish when a silicon has a next nearest neighbour titanium (i.e. TiO_4). Observed resonances additional to the framework Q^4 silicon must be from incomplete condensation of the structure either due to Q^3 -OH or titanium in a network modifying role (i.e. TiO_6).

^{17}O NMR resonances were reported for the first time from Ta-O-Ta and Ta-O-Si linkages.¹⁰ In pure Ta_2O_5 , resonances appear at ~ 280 and 440 ppm from Ta-O-Ta corresponding to coordinations OTa_2 and OTa_3 respectively. In gel formation of Ta_2O_5 the proportion and exact positions of these resonances varies with heat treatment. Ta-O-Si groups show a ^{17}O resonance at around 160 ppm.

In $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ materials the distinct resonances from Ti-O-Ti, Ti-O-Si and Si-O-Si were used to infer whether or not nanoscale phase separation occurred in a preliminary study.[‡] The work here reinforced the view that ^{17}O is a direct and sensitive way of detecting phase separation. As an example the effect of complexing the titanium precursor with acac even at 41 mol% TiO_2 in the initial gel there is no Ti-O-Ti bonding (Fig. 1). On heating the ^{17}O NMR data shows that although Ti-O-Si bonding persists some phase separation occurs.

The ^{17}O resonances should allow identification of the structural units present to be identified. In $\text{TiO}_2\text{-SiO}_2$ materials prepared with acac two distinct Ti-O-Si resonances are observed in the initial gel at 110 and 250 ppm. There is still some debate as to the exact identity of these, but they could correspond to Si-O-TiO₅ and Si-O-TiO₃. The assignment of the 250 ppm peak to Si-O-Ti with titanium substitutionally in the SiO_2 framework is unequivocal. The quantitative integrity of the spectra was investigated by recording spectra at applied magnetic fields of 5.6 to 14.1 T.¹⁴ This showed that peak integration gave accuracy for quantification of the different species of $\sim \pm 5\%$. It also showed that the widths of the distinct resonances were determined by different interactions (*viz.* chemical shift dispersion and second-order quadrupolar) and that their differing field dependencies need to be factored into quantifying the spectra. The last few years has witnessed a considerable increase in the number of papers reporting ^{17}O NMR data. The work in this project should find widespread application in interpreting such ^{17}O NMR data.

***In situ* X-ray diffraction**

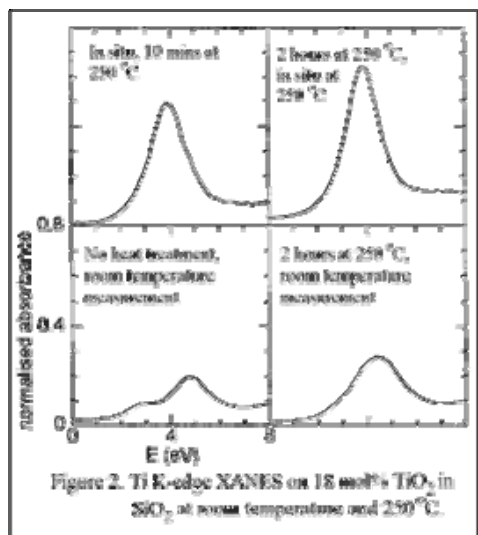
Diffraction data allows structural evolution to be followed, and to be able to follow structural evolution in the amorphous solids especially in a time-resolved fashion would be extremely helpful for understanding the sol-gel process. There have been very few such studies using the diffuse diffraction from amorphous solids. The development of curved image plates simultaneously collecting across the whole angular range has reduced collection times to minutes instead of hours. The camera geometry allows data to be collected to high momentum transfer, providing the good real space resolution necessary to study amorphous materials. Since the structure of $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ was well characterised by other methods it provided an ideal test of the approach. The *in situ* data showed significant TiO_4 formation at 210°C with by 310°C the titanium becoming fourfold coordinate within the framework which remained stable up to 500°C.⁸ With recent developments at the ESRF with using the higher flux at higher energies and state of the art solid state area detectors means that an even greater Q-range combined and finer time resolution is now possible. An initial experiment, using a solid state detector, and was applied to recently undertaken on $\text{Ta}_2\text{O}_5\text{-SiO}_2$ materials.¹⁶

Application of XANES and *in situ* studies

The height and the position of the pre-edge peak of Ti K-edge XANES is known to be a sensitive indicator of the coordination of titanium. In this project calibration of the Ti K-edge data was extended by looking at additional reference compounds. This confirmed that the fingerprinting approach could be used successfully to identify three distinct titanium coordinations within these materials and follow their conversion *ex situ*. This study was the first time that such coordination changes have been unambiguously followed and described by XANES. Similar work was also developed for the Zr K-edge.^{7,9} Discrimination of the local coordination is less sensitive for Zr than for Ti but by comparison with model compounds the XANES can provide information about the changes in the local coordination of Zr in amorphous materials.

The speed of acquiring XANES data means that *in situ*, real time experiments can be carried out. In an $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ which has had not had heat treatment TiO_6 is dominant. Yet even after only 10 minutes at temperature most of this has converted to TiO_4 (Fig. 2). On cooling and exposure to ambient

atmosphere most of the TiO_4 reverts back to TiO_6 through interaction with moisture..³ Prolonged heat treatment increased the amount of TiO_4 that is part of the SiO_2 framework and is inaccessible to moisture. It is TiO_4 sites that are accessible and show rapid conversion that are likely to be catalytically active. Similar behaviour was seen in for Zr addition to SiO_2 indicating that water tries to overcome the coordinatively unsaturated state imposed by the SiO_2 network..⁹



3.2. Systems Studied

$(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$. In sol-gel prepared samples with low x (e.g. 0.08) titanium is dispersed throughout the network and all becomes incorporated within the silica framework after heat treatment. At $x > 0.3$ unheated samples contain phase separated TiO_6 with Ti-O-Ti bonding that convert to anatase on heating. Even heating to 750°C leaves some microporosity with phase separated domains of anatase in an SiO_2 matrix with some dissolved titanium. SAXS and WAXS agree on the domain sizes..¹¹ Behaviour of intermediate compositions (e.g. $x=0.18$) is complex with in the initial gel despite the presence of some Ti-O-Ti linkages moderate heating disperses these so that titanium is only involved in Ti-O-Si bonding..¹⁴ SAXS only shows some phase separation at elevated temperatures. Heat treatment converts TiO_6 sites into framework

TiO_4 sites. There is no evidence of any TiO_5 forming in these sol-gel samples, in complete contrast to melt-quenched glasses where TiO_5 is postulated to be a common species. Modification of the reactivity of the titanium precursor with acac greatly reduces/modifies its reactivity and discourages Ti-O-Ti formation so that even at $x=0.41$ in the initial gel there is no Ti-O-Ti bonding..² Then with heat treatment in acac treated samples the amount of titanium remaining atomically mixed within the SiO_2 matrix is increased compared to when no acac is used in the preparation.

$(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$. Although zirconium is soluble within an SiO_2 matrix this study has shown that its role is very different to titanium. Rather than becoming part of the framework, zirconium keeps a high coordination number and acts as a network modifier. As this study progressed refinements of the data showed the local structure is better described as like Zr n-propoxide rather than like cubic ZrO_2 ..⁹ At higher Zr contents a lot of the Zr is present in an amorphous tetragonal-like prepursor like phase but with $x = 0.4$ the amount of Zr-O-Si bonding exceeds that in $x = 0.1$. The combination of techniques was shown to be crucial for detecting nanoscale phase separation that influences the properties of these materials. At $\text{Zr} \leq 0.2$ no phase separation occurs but the Zr causes distortion of the SiO_2 lattice with some Zr-Zr clustering occurring.

$(\text{Ta}_2\text{O}_5)_x(\text{SiO}_2)_{1-x}$. It was shown that Ta acts as a network modifier, and in the amorphous phases studied here prefers to be TaO_5 , a very unusual coordination for Ta in crystalline compounds. Phase separation occurs at $x > 0.11$ and was correlated with an IR feature at 960 cm^{-1} that can be used to routinely monitor phase separation..¹⁰

3.3. Optimisation of catalytic properties.

The structural work suggested that maximum catalytic activity would be achieved by maximising the number of isolated $\text{TiO}_6 \leftrightarrow \text{TiO}_4$ reversible sites as detected by XANES. This meant working with a $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ sample and SAXS showed that the pore volume was preserved by washing with

heptane prior to drying to give surface areas of up to $450 \text{ m}^2\text{g}^{-1}$.¹² The catalytic activity was monitored through epoxidation of cyclohexene with tert-butyl hydroperoxide and these samples had excellent selectivity (> 90%) and reasonable conversion percentages (~ 20 %). The detailed structural work using XANES, EXAFS and ^{17}O MAS NMR showed that the intensity of the Si-O-Ti FTIR signal at 960 cm^{-1} was again a good indication of the dispersion of titanium in active sites, and hence of the catalytic activity.

4. Project Management

Both investigators spent the time stated on the original application involved directly with the project and jointly managed the research programme. One year into the grant the principal investigator moved institutions but this did not hinder progress and the project proceeded largely as outlined in the original project plan with only minor amendments. Full use was made of electronic communication between the team and quarterly team meetings of the whole research team were held alternately at Kent and Warwick. In all experiments at central facilities team members from both sites were involved. Expenditure and attendance at conferences was as outlined in the original case.

5. Personnel and Training

The project directly employed directly a PDRA and a research student. The PDRA (Dr D.M. Pickup) came with excellent synthetic skills and some experience in scattering techniques. This project used and enhanced these skills, and additionally introduced him to other techniques especially solid state NMR and FT-IR. The PDRA was in charge of commissioning and running the new FT-IR equipment and coordinated many of the central facilities experiments. The NMR experience gained through this project allowed the PDRA to take up a new EU funded research position at Kent in solid state NMR. The student (Mr G.W. Wallidge) is a physics graduate and obtained extensive training in sample preparation, and in using diffraction techniques to investigate the structure of amorphous materials. Currently his thesis is being written and it is anticipated that this will be submitted in December 2000. Presentational skills of these staff were developed through five presentations at meetings (2 talks, 3 posters, see appendix).

The opportunities provided by this grant were also exploited by other associated workers. Two PhD students on EPSRC Quota awards were partially involved in the work. R. Anderson, who submitted her thesis in December 1998 entitled , "A study of the atomic scale structure of novel glass materials", and M.A. Holland (1998-2001) is currently engaged on a study of the structure-catalytic properties relations of these materials. Other research assistants have also used the opportunities provided by the grant with Dr G. Mountjoy largely responsible for the development of the ideas related to XANES characterisation which proved highly successful. Experience at central facilities was also gained by Dr J.M. Cole and Dr C. Gervais. We believe that this represents good use of the research training opportunities provided by this grant in important materials preparation and core physical science skills. Such training should have given these workers highly desirable competencies that make them widely attractive for employment. This materials-physics interface expertise developed here also provides good undergraduate project training.

6. Dissemination and Relevance to Beneficiaries

Twelve papers have already appeared or been accepted in fully refereed, international journals. These have been spread across physics/chemical physics and specialised technique journals to those that make direct contact with the specific beneficiaries outlined in the original proposal; solid-state chemists and materials scientists interested in sol-gel processes. In disseminating the research at conferences a similar

attitude was adopted with both specialised technique-based and materials- oriented meetings being attended. In particular, given the relevance of this work to understanding sol-gel prepared materials, we have supported meetings of the UK-Ireland Sol-Gel Group. Parts of this work have been incorporated into a non-specialist talk entitled "Glass: a new look inside" by Prof. Newport that has been given at events aimed at public understanding of science e.g. IOP and SET regional talks for the general public and University open days/lectures.

This work, on building comprehensive experimental data sets to understand the structure of amorphous materials, has shown that much of the work done in the past was ambiguous and needs reinterpretation. The structural significance of features in data from the different techniques is now better understood. It can be anticipated that more use will be made by materials scientists in the future of ^{17}O MAS NMR, XANES and *in situ* X-ray diffraction and absorption techniques to understand materials. There is also much better calibration of features in the FTIR spectra which can be directly related to catalytic activity.

7. Collaborations and Future Work

This project demonstrated that the synergy of applying complementary techniques gives much more confidence in the structural picture that can be developed for amorphous materials. Given that this has called into question many of the structural pictures in the literature of these widely studied doped silica systems, these could usefully be studied even further. Funding through a joint pair of grants (GR/N64141, GR/N64267) will allow more sophisticated experiments to further refine and improve these structural models. Experiments will include novel isotope difference neutron scattering experiments and development of solid state NMR of the metals, especially $^{47,49}\text{Ti}$. The preliminary work carried out in the current grant showed the feasibility of *in situ* experiments and this gets closer to problems associated with materials processing so will now be more vigorously pursued. The use of more intense, higher coherence X-ray sources such as the ESRF also offer new possibilities such as much improved time resolution for kinetic studies and alternative methods of identifying atomic environments through anomalous X-ray scattering.

An intention of this project was to establish direct links with the target beneficiaries which has been achieved. A joint CNRS/Royal Society grant allowed exchange visits to the laboratory of Dr F. Babonneau, an international authority on sol-gel materials. Dr Babonneau was very interested in applying some of the developments here. Through a Marie Curie fellowship to Dr C. Gervais the ^{17}O NMR developed in this project has been taken further by examining quantitatively ^{17}O NMR spectra to examine the effect of functionalisation on phase separation. RJN add new EU research fellow. Also Johnson Matthey Research is interested in the methodology developed here to look at metal centres in silica matrices. Currently they are funding a PhD CASE award looking at the effect of vanadium in zircon glazes. Further an important collaboration has been started with Dr S.C.E. Tsang of the Catalysis Research Centre of the Department of Chemistry at the University of Reading. Given that titanium in silica is important in catalysis technology, this project has provided new information about the different titanium sites present in such materials. The work on relating structural detail to catalytic properties has already led to one joint publication with Dr Tsang and there is continuing collaboration on developing *in situ* measurements of catalytic sites. A. van Putten is funded by Utrecht University to spend a year (9/2000-8/2001) learning from us, with a particular focus on controlling pore size distributions in the catalytically active materials.

Summary GR/L28647

Development of an Advanced Characterisation Methodology for Gel-Produced Materials

Overview

Extensive sets of complementary experimental data were collected on sol-gel prepared binary mixtures of SiO₂ with TiO₂, ZrO₂ and Ta₂O₅. The techniques used included diffraction (X-ray and neutron), multinuclear solid state NMR, X-ray absorption (EXAFS and XANES), small angle scattering (SAXS) and FT-IR. This provided some of the most comprehensive structural data sets on such amorphous materials ever collected, allowing the differing behaviours of Ti, Zr and Ta in silica to be examined, and elucidating how these amorphous structures develop with heat treatment. The information from the characterisation methodology developed here emphasised that many existing studies based on a more limited experimental approach have often been misled into incorrect structural models. The improved knowledge of structure has allowed more certain calibration of features in the FT-IR spectra improving the utility of FT-IR for solid state chemists and materials scientists interested in characterising such materials. As the structure is now better understood it was desirable to begin relating structure to important technological properties such as catalysis, and this should have widespread utility for researchers developing these materials.

Technique Developments

- ¹⁷O solid state NMR could easily separate Si-O-Si, Si-O-Ti and Ti-O-Ti, which was used to detect phase separation and could even distinguish different types of Si-O-Ti. The first ¹⁷O data from Ta-O-Ta and Si-O-Ta were reported. All this indicated the sensitivity of ¹⁷O NMR as a probe of oxide-based solids which should find increasingly wide usage.
- The Ti K-edge pre-edge feature was developed as a very sensitive probe of the titanium coordination in these materials; the speed of data collection means that *in situ*, real-time studies can be carried out. Some sites show rapid TiO₄ ↔ TiO₆ conversion on interaction with moisture. Zr XANES is less discriminatory of the local environment, it provided new information about structural changes.
- Diffuse diffraction from amorphous materials is still little used to provide structural information, but it was shown to provide important insights into the overall network, and some exploratory *in situ* X-ray diffraction was reported – the latter being of significant potential future use. The complementary scattering of neutrons and X-ray helps to identify specific correlations.

Materials Information

- Several distinct titanium sites could be identified. In the porous glass formed those directly linked to the catalytic behaviour were TiO₆ that convert to TiO₄ on heating. Sites permanently converted into phase separated TiO₂ or stable TiO₄ within the silica network reduce catalytic effectiveness.
- Titanium acts as both a network former and modifier in SiO₂ but with no evidence in sol-gel formed samples of significant TiO₅-content, in marked contrast to comparable melt-quenched glasses.
- Zirconium has high solubility in SiO₂ (i.e. no detectable phase separation at < 20 mol% ZrO₂) but has a very different role to titanium, being exclusively a network modifier.
- Tantalum acts as a network modifier in SiO₂ and prefers to take on an unusual TaO₅ coordination.
- (TiO₂)_{0.18}(SiO₂)_{0.82} samples washed in heptane preserved the surface areas of 450 m²g⁻¹ and showed maximum catalytic activity for these samples.

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Appendix: Publications, Talks and Posters

Fully refereed International Journals (chronological order)

(a) published and accepted for publication

1. Structure of $(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$ xerogels ($x = 0.1, 0.2, 0.3$ and 0.4) from FT-IR, ^{29}Si and ^{17}O MAS-NMR and EXAFS. D.M. Pickup, G. Mountjoy, G.W. Wallidge, R.J. Newport and M.E. Smith, *Phys. Chem. Chem. Phys.*, 1 (1999) 2527-2533.
2. A structural study of $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ ($x = 0.18, 0.30$ and 0.41) xerogels prepared using acetylacetone. D.M. Pickup, G. Mountjoy, G.W. Wallidge, R. Anderson, J.M. Cole, R.J. Newport and M.E. Smith, *J. Mater. Chem.*, 9 (1999) 1299-1305.
3. In-situ high temperature XANES observations of rapid and reversible changes in Ti coordination in titania silica xerogels. G. Mountjoy, D.M. Pickup, G.W. Wallidge, J.M. Cole, R.J. Newport and M.E. Smith, *Chem. Phys. Lett.*, 304 (1999) 150-154.
4. Comment on "atomic ordering in $x\text{ZrO}_2:(1-x)\text{SiO}_2$ xerogels ($x = 0.3, 0.5$) by X-ray diffraction and reverse monte carlo simulations". G. Mountjoy, D.M. Pickup, M.E. Smith and R.J. Newport, *J. Mater. Sci. Lett.*, 18 (1999) 1553.
5. A XANES study of Ti coordination in heat treated $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ xerogels. G. Mountjoy, D.M. Pickup, G.W. Wallidge, R. Anderson, J.M. Cole, R.J. Newport and M.E. Smith, *Chem. Mater.*, 11 (1999) 1253-1258.
6. Recent advances in experimental solid state NMR methodology for half-integer spin quadrupolar nuclei. M.E. Smith and E.R.H. van Eck, *Prog. NMR Spectrosc.*, 34 (1999) 159-201.
7. The effect of zirconia content on the structure of zirconia-silica xerogels as determined by x-ray and neutron diffraction and Zr K-edge EXAFS and XANES. G. Mountjoy, R. Anderson, R.J. Newport and M.E. Smith, *J. Phys.: Condens. Matter.*, 12 (2000) 3505-3519.
8. In-situ high temperature X-ray scattering measurements on a $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ xerogel using a curved image-plate. D.M. Pickup, G. Mountjoy, M.A. Roberts, G.W. Wallidge, R.J. Newport and M.E. Smith, *J. Phys.: Condens. Matter.*, 12 (2000) 3521-3529.
9. Changes in the Zr environment in zirconia-silica xerogels with composition and heat treatment as revealed by Zr K-edge XANES and EXAFS. G. Mountjoy, D.M. Pickup, R. Anderson, G.W. Wallidge, M.A. Holland, R.J. Newport, and M.E. Smith, *Phys. Chem. Chem. Phys.*, 2 (2000) 2455-2460.
10. Structure of $(\text{Ta}_2\text{O}_5)_x(\text{SiO}_2)_{1-x}$ xerogels ($x = 0.05, 0.11, 0.18, 0.25$ and 1.0) from FTIR, ^{29}Si and ^{17}O MAS NMR and EXAFS. D.M. Pickup, G. Mountjoy, M.A. Holland, G.W. Wallidge, R.J. Newport and M.E. Smith, *J. Mater. Chem.*, 10 (2000) 1887-1894.
11. Synthesis, characterisation and performance of $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ xerogel catalysts. M.A. Holland, D.M. Pickup, G. Mountjoy, S.C.E. Tsang, G.W. Wallidge, M.E. Smith and R.J. Newport, *J. Mater. Chem.*, (accepted).

(b) submitted and in preparation

13. Using in-situ quEXAFS and XANES measurements to follow the calcination of a $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ sol-gel. D.M. Pickup, G. Mountjoy, M.A. Holland, G.W. Wallidge, R.J. Newport and M.E. Smith, *J. Phys.: Condens. Matter.*, (submitted).
14. Advanced physical characterisation of the structural evolution of amorphous $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ sol-gels. G.W. Wallidge, R. Anderson, G. Mountjoy, R.J. Newport, D.M. Pickup and M.E. Smith, *Phys. Rev B*, (submitted).
15. EXAFS/XANES of $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ sol-gel materials. M.A. Holland, G. Mountjoy, R.J. Newport and M.E. Smith, *Phys. Chem. Chem. Phys.* (in preparation).
16. An X-ray diffraction study of sol-gel formed $(\text{Ta}_2\text{O}_5)_x(\text{SiO}_2)_{1-x}$. D.M. Pickup, M.A. Holland, C. Gervais, V Honkimaki, R.J. Newport and M.E. Smith, *J. Phys.: Condens. Matter* (in preparation).

Published conference papers

17. An EXAFS study of silica:titanium sol-gels. R. Anderson, G. Mountjoy, M.E. Smith and R.J. Newport, *J. Non-Cryst. Solids*, **232-234** (1998) 72-79.
18. Spectroscopic characterisation of mixed titanium-silica xerogel catalysts. M.A. Holland, D.M. Pickup, G. Mountjoy, S.C.E. Tsang, G.W. Wallidge and M.E. Smith, *Mat.Res.Soc. Symp.Proc.*, **590** (2000) 77-82.
19. Synchrotron-based studies of transition metal incorporation into silica-based sol-gel materials. G. Mountjoy, D.M. Pickup, M.A. Holland, G.W. Wallidge, R.J. Newport and M.E. Smith, *Mat.Res.Soc. Symp.Proc.*, **590** (2000) 83-88.
20. In-situ studies of the processing of sol-gel produced materials using SAXS, curved image plate XRD and XANES. D.M. Pickup, G. Mountjoy, R.J. Newport, M.E. Smith, G.W. Wallidge and M.A. Roberts, *Mat.Res.Soc. Symp.Proc.*, **590** (2000) 119-124.

CCLRC Reports

21. The structure of silica:titanium and zirconia titanium sol-gel materials. R. Anderson, G. Mountjoy, M.E. Smith and R.J. Newport, *SRS Annual Report 1996-1997*, 60-61.
22. In-situ high temperature XANES observations of rapid and reversible changes in the Ti coordination in titanium-silica xerogels. D.M. Pickup, R.J. Newport, G. Mountjoy, M.E. Smith and G.W. Wallidge, *SRS Annual Report, 1997-1998*, 256-257.
23. The structure of Ti and Zr doped SiO_2 sol-gels. D.M. Pickup, R.J. Newport, G.W. Wallidge and M.E. Smith, *SRS Annual Report, 1997-1998*, 288-289.
24. The structure of novel binary sol-gel glasses. R.J. Newport, R. Anderson and W.S. Howells, *ISIS Experimental Report no. RB7573, 1997. 2325. The structure of $\text{ZrO}_2\text{-SiO}_2$ sol-gels as a function of zirconia content. R.J. Newport, D. Pickup, J.M. Cole and G.W. Wallidge, ISIS Experimental Report no. RB9211, 1998. Page??*
25. Using in-situ quEXAFS and XANES measurements to follow the calcination of a $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ aerogel. D.M. Pickup, R.J. Newport, G. Mountjoy, M.A. Holland, M.E. Smith and G.W. Wallidge, *SRS Annual Report, submitted, May 2000*.
26. Tantalum oxide:silica sol-gels: Their structural evolution with calcination. R.J. Newport, M. Holland, D.M. Pickup and G.W. Wallidge, *ISIS Experimental Report no RB11339, submitted, May 2000*.

Conference Presentations (presenting author only given).

(a) Invited

1. LAD and novel materials. R.J. Newport, LAD, 1981-1998: the first ISIS diffractometer, Abingdon, March 1999.
2. Characterising disordered solids by ^{17}O NMR M.E. Smith, American Chemical Society Annual Meeting, New Orleans, August 1999.
3. ^{17}O solid state NMR characterisation of Si-O-Ti linkages M.E. Smith, BRSG Easter meeting, Cambridge, April 2000.
4. Metal environments in silica-based sol gel materials and in phosphate glasses. R.J. Newport 'The structure and dynamics of the liquid and glassy states: X-ray and complementary methods', ESRF, Grenoble, May 2000.

(b) Contributed

5. An EXAFS study of silica:titanium sol-gels. R. Anderson, NCM7. Sardegna, Italy, September 1997.
6. Strategy for characterisation of Ti and Zr doped silica sol-gels. D.M. Pickup, UK-Ireland Sol-Gel Group Meeting, Imperial College, London, March 1998.
7. The structural evolution of titania-silica gels with heat treatment. G.W. Wallidge, UK-Ireland Sol-Gel Group Meeting, Imperial College, London, March 1998.
8. Structural evolution with heating of $\text{TiO}_2:\text{SiO}_2$ sol-gels. G.W. Wallidge, Society of Glass Technology New Researchers' Meeting, University of Warwick, April 1999.
9. Spectroscopic characterisation of mixed titania-silica xerogel catalysts. M.A. Holland, UK-Ireland Sol-Gel Group Meeting, Loughborough University, June 1999.
10. An advanced characterisation methodology for sol-gel materials. M.E. Smith, UK-Ireland Sol-Gel Group Meeting, Loughborough University, June 1999.
11. Structural evolution with heating of $\text{TiO}_2:\text{SiO}_2$ sol-gels. G.W. Wallidge, UK-Ireland Sol-Gel Group Meeting, Loughborough University, 1999.
12. Spectroscopic characterisation of mixed titania-silica xerogel catalysts. M.A. Holland, MRS Fall Meeting, Boston, November 1999.
13. In-situ studies of the processing of sol-gel produced materials using SAXS, curved image plate XRD and XANES. G. Mountjoy, MRS Fall Meeting, Boston, November 1999.
14. Synchrotron-based studies of transition metal incorporation into silica-based sol-gel materials. R.J. Newport, MRS Fall Meeting, Boston, November 1999.
15. Using in-situ synchrotron measurements to follow the calcination of a $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ sol-gel. D.M. Pickup, 'The structure and dynamics of the liquid and glassy states: X-ray and complementary methods', ESRF, Grenoble, May 2000.
16. Spectroscopic characterisation of mixed titania-silica xerogel catalysts. M.A. Holland, 'The structure and dynamics of the liquid and glassy states: X-ray and complementary methods', ESRF, Grenoble, May 2000.