Commentary on Materials Discussion 5: Porous Materials and Molecular Intercalation

This issue of *Journal of Materials Chemistry* collects together papers which were presented at Materials Discussion 5: Porous Materials and Molecular Intercalation—a conference organised by the Royal Society of Chemistry. The meeting took place at the Residencia de Estudiantes at the CSIC (the National Research Council of Spain) Campus in Madrid during 22–25 September 2002. Around ninety delegates from fourteen countries, including Japan and the United States, participated. Topics such as new host inorganic solids, intercalation properties and surface reactivity involving layered and nanoporous materials were featured. Several overviews, in the form of keynote lectures, were given by selected prominent international experts, illustrating recent developments in specific areas. These are reproduced in this issue as Feature Articles. Additionally, the full papers featured here were presented as five minute lectures with a full fifteen minutes of discussion afterwards. More general discussion on the overall topics of the different sessions was also heard. We summarise here the most relevant features arising from these discussions between the delegates.

Pilar Aranda and Eduardo Ruiz-Hitzky

The meeting started with a Plenary Lecture entitled "Aluminosilicate Mesostructures with Improved Acidity and Hydrothermal Stability" presented by Prof. T. J. Pinnavaia from Michigan State University and chaired by Prof. J. M. Serratosa from the CSIC. The recently discovered mesoporous aluminosilicates, prepared *via* different assembly pathways, have emerged as materials of increasing promise for applications in selective adsorption and catalytic processes. Prof. Pinnavaia (see p. 3179) focused his attention on this subject towards the use of nanoclustered zeolite seeds as precursors for direct assembly or in post-synthesis grafting reactions. He concluded that the zeolite seed precursors improve hydrothermal stability and acidity, regardless of the assembly pathway. The use of the MCM-41-type solids assembled from diblock, triblock and alkylammonium ion surfactants at basic pH are the most stable of the resulting aluminosilicate mesostructures, whereas solids assembled through acidic pathways (*e.g.* MCF, SBA-15 analogues) and wormholes assembled from amines (*e.g.* HMS, TUD-1 analogues) exhibit less improvement in stability and acidity. This seeding approach will provide a useful procedure for improving current conventional cracking catalysts, such as zeolites, because the larger pore size provided by these mesoporous oxides overcomes the significant problems of molecular access to the active centres.

The first session, devoted to **Micro- and Mesoporous Solids**, was chaired by W. Jones and J. Sanz. The papers considered subject matters concerning the synthesis and characterisation of porous solids. Four distinct materials were considered: synthetic hectorites (K. A. Carrado, see p. 3228), carbons (J. M. Tascón, see p. 3213), phosphonates (G. B. Hix, see p. 3220) and silicas (R. E. Morris, see p. 3208), relating to applications ranging from adsorption to catalysis. The distinction between local structure and long range arrangement was an important aspect. Only in the case of the phosphonate materials was it possible to obtain full three-dimensional structures. Although the thermal stability of the materials was considered an important aspect for study, it was clear that among the range of potential applications, some do not always require thermal stability. There are many processes (*e.g.* in pharmaceutical chemistry and specialty chemicals) where low temperature synthesis conditions are entirely acceptable, and indeed desirable. Specific questions were

DOI: 10.1039/b209648j

also addressed to each of the material types. In the case of microporous activated carbon fibres, it is critical to establish what physical picture could be envisaged to create such very high surface areas. Suggested ideas included effects related to stacking of disordered 'graphine' sheets. In the case of silica materials based on polysilsesquioxanes, improvements in thermal stability are crucial. Possible solutions, such as the replacement of carbon linkages by siloxane bridges, were proposed. Regarding phosphonates, questions mainly concerned the design of microporous materials from this family of compounds. The most likely guideline was thought to be the presence of non-octahedral cations within the framework. In relation to synthetic hectorites, it was pointed out that an important contribution to porosity/surface area measurements may well come from the existence of an amorphous silica phase, in possible agreement with the measured Si/Mg ratios. Thus, one salient question which could not be conclusively answered was how to detect amorphous phases in the presence of crystalline materials.

The session on **Inorganic Solids as Hosts for New Intercalations**, chaired by T. J. Pinnavaia and C. Detellier, described four host systems for new intercalation processes, namely, layered double hydroxides (D. O'Hare, see p. 3191), layered nickel hydroxide (N. Jouini, see p. 3238) , mesoporous titania (G. Ouvrard, see p. 3245) and layered zirconium phosphonate (R. Vivani, see p. 3254). The keynote lecture on LDHs as hosts by Prof. O'Hare focused on two fundamental processes: (i) the staging of organic/inorganic intercalated species which occurs in interlayer space of the LDHs and (ii) the kinetics of anion replacement within the interlayer space. The staging phenomenon is thermodynamically driven, suggesting that charge distribution in the structure is responsible for this novel process. The kinetics and mechanism of organic anion intercalation can be strongly dependent on the molecular size and shape of the ion, making it possible to use intercalation phenomena to purify organic anion mixtures, particularly isomeric mixtures that are difficult to separate using conventional ion-exchange resins. Additional uses of LDH intercalation compounds include the design of slow release agents for the delivery of bio-active molecules. The intercalation of carboxylate anions into $Ni(OH)_2$ occurs through the replacement of hydroxyl groups in the brucite-like sheets. The grafted carboxylate ions can be solvated by polar molecules, allowing swelling of the layered material. This changes the relative magnitudes of the magnetic coupling between nickel centres within and between the layers, leading to strongly anisotropic magnetic behaviour. Mesoporous titania is electrochemically active, allowing for the intercalation of Li^+ ions under an applied electrical potential. Such intercalation behaviour may find application in the design of rechargeable Li batteries. Although layered zirconium phosphonates have been known for several decades, their intercalation properties are limited by the large volumes occupied by the organic groups on the phosphonate centre. However, the layered structure derived from bifunctional phosphonates, in which there are two phosphonates per organic group, show very different intercalation behaviour. The kinked conformation of the organic chain should improve the intercalation properties by allowing better access to the gallery regions of the structure. This last type of new organic–inorganic solid generated a constructive debate concerning the possibilities of developing novel related materials and their subsequent applications. In this context, Prof. U. Costantino extended the data available on these materials, showing the generality of the synthetic routes and the potential for materials innovation.

The session devoted to **Functionalisation of Porous Materials**, chaired by D. O'Hare and M. Ogawa, included three discussion papers concerning organic–inorganic hybrid materials involving macroporous (A. Stein, see p. 3261), mesoporous (Y. Fukushima, see p. 3275) and microporous (P. A. Sermon, see p. 3278) materials. The macroporous materials reported by Dr Stein contain thiol groups located at accessible pores that are able to adsorb heavy metal ions, such as lead and mercury, from aqueous solutions. In addition, these functionalised solids were successfully reused retaining about 75% of their initial activity. Questions concerning the immobilisation of metals such as gold, were raised in view of the potential applications of such materials in electrochemical devices. Similar systems based on silica are feasible and compare well with thiol-functionalised mesoporous sieves. As explained by Dr Stein, the limitation involves the combination of optical changes which accompany metal uptake. Metals could indeed be absorbed, but optical changes were dominated by shrinkage of the framework, rather than changes in the effective refractive index of the walls. Inclusion of chlorophyll *a* into FSM mesoporous silicas leads to unique pore size sensitive adsorption behaviour, which caused controversial interpretations among the delegates. Questions related to the orientation of molecules inside the mesopores, the external *vs.* internal adsorption ratio and the search for techniques which could provide information on the disposition of molecules inside the pores were extensively discussed. The paper on organic–inorganic materials based on macrocycles entrapped on silica prepared by the sol–gel technique revisited a known subject for the purpose of preparing membranes for ion sensing. The increased porosity of the systems reported here was suggested to be a potential problem as regards leaching of the sensing agents. Some of the discussion focused on the difficulties of characterising functionalised porous materials. The consensus was that a combination of methods is required, particularly spectroscopic and absorption measurements.

The session on **Organic Reactions on Porous Supports** was chaired by D. Jones and A. Stein. New opportunities for organic transformations using alternative energy sources and reaction media, and on supports such as alumina, silica or clays, were described in the keynote lecture given by Dr R. S. Varma (see p. 3199). A wide range of different types of reactions that can benefit from this approach were described, and the variety of applications, flexibility and simplicity were emphasised. The discussion addressed, in particular, the role played by the support and its surface, its influence on the outcome of the reaction, the differences in selectivity with respect to reaction under conventional conditions and the possible influence of metals. Well-characterised surfaces could be of interest in this context. Improved *p*-selectivity in the nitration of aromatics using N_2O_4 and in the presence of zeolite was discussed (K. Smith, see p. 3285), with the particular advantage that the reaction under such non-conventional conditions is stoichiometric with respect to N_2O_4. The possible shape selectivity role of the zeolite was discussed and unusual active species possibly present on the zeolite pores were suggested. The effect of the support was also the subject of discussion in the paper presented by Dr J. A. Mayoral (see p. 3290). Here, Laponite and Nafion–silica composites were chosen to mimic the homogeneous reaction medium for conversion and chiral selectivity. The nature of the interaction and the importance of the loading of bis(oxazoline)–copper complexes were discussed. In the contribution on new noble metal (Rh, Ru, Ir) catalysts obtained by co-precipitation with Mg and Al precursors (F. Basile, see p. 3296), the sites of the heteroatom (Rh, Ru, Ir) in the cationic layers was the particular object of discussion, with questions addressing the limitation of the amount of metal that could be located without phase segregation. In summary, the main discussion points from this session centred on: (i) selectivity and reaction pathways in processes employing non-conventional reaction media or non-conventional energy sources, and what their influence is in the formation of products different from those obtained under conventional conditions, (ii) the importance/role of supports, such as what "a clay" actually is and including the importance of its composition, (iii) the importance of the nature of the support surface (polarity, water content, and magnetic and electrical behaviour), in particular for microwave-assisted reactions, (iv) application of *in situ* characterisation methods for fast reactions, (v) use of supports with well-characterised surfaces (known reactive sites) to help in the determination of mechanism and the nature of the surface interactions. All of these emerging ideas were directed toward a better understanding of reactions and their control based on support selection and the type of energy source to be applied.

The session on **Organo-clays and Nanocomposite Materials**, chaired by R. Schoonheydt and K. A. Carrado, included two papers on polymer nanocomposites using different inorganic materials: layered Ca–silicate hydrated cement precursors (H. Van Damme, see p. 3308) and LDHs (F. Leroux, see p. 3324). There were also two papers on photoactive molecules within magadiite (M. Ogawa, see p. 3304) and LDHs (U. Costantino, see p. 3316). Efforts to exfoliate the Ca–silicate hydrates, which possess much higher charge densities than conventional clays, were the focus of the next talk. The difficulty of reproducibly preparing the highly complex Ca–silicate hydrate cement-like materials was stressed. Modelling of the interfacial region between the high charge Ca–silicate hydrate and LDH inorganic systems and the polymer was one topic raised in the discussion period. It is expected that the differences in charge density and, perhaps, layer rigidity will play a large role in determining the physical and chemical properties of such nanocomposites. Also of note is the trend towards crystallising or templating layered inorganic components directly within a polymer-containing solution. The focus of the paper on polymer–LDHs was not directly on exfoliation, however. Rather, Dr Leroux detailed successful preparation of better ordered polystyrene–LDH nanocomposites than has been reported previously. Discussions regarding photoisomerisation of azobenzene in the interlayer space of magadiite included aspects related to the shifts of the d_{001} line in XRD patterns, which are crucial to the observation of the photoisomerisation, and whether higher order reflections and/or time-dependent XRD measurements could be of use. The latter allow the evolution of the spacing of magadiite to be followed in parallel with the spectroscopic measurements. Residual water and ethanol, used as a solvent, might change the microenvironment of azobenzene in the interlamellar space, thus influencing the kinetics and, hence, the mechanism of the reaction. As the molecules are presented as a closely packed layer in the interlamellar space, the question of whether they should be considered as monomers or as aggregates was addressed. It was pointed out that the spectra indicate that they are monomers. Concerning the organic chromophores co-intercalated into LDHs, the interpretation of the various crystalline phases was not straightforward and several factors, such as the homogeneous distribution of dyes in the interlamellar space, segregation, interstratification and turbostratic structures, must be taken into account. It seems that donor–acceptor interactions are also dependent on the molecular organisation in the interlamellar spaces and on the distance between donor and acceptor molecules. Finally, the type of structure that can be obtained in co-intercalation processes was thought to depend on the mechanism of intercalation. Thus, a key question is whether the process is kinetically or thermodynamically controlled. In the latter case, the minimum energy structure is obtained, whereas in the former this is not necessarily the case. Mixing salts of the dyes to ascertain whether a mixed salt emerges might be a strategy to determine whether homogeneous distribution, interstratification or something else can occur in the interlamellar space.

The last session, devoted to **Novel Technologies and Applications**, was chaired by H. Van Damme and M. Hernández-Vélez. The four papers discussed in this session covered selected examples of device- or process-oriented technical and material developments. In the first paper (R. Schoonheydt, see p. 3268) an innovative use of the Langmuir–Blodgett technique was presented. Well-ordered monolayers and multilayers of monodisperse sub-micrometric silica particles were deposited on glass by this technique. Moreover, there is clear evidence that a deposit only a few monolayers thick is sufficient to generate an optical band gap in the region predicted by theory. Thanks to its flexibility, this attractive technique might become a serious competitor to the existing methods for the preparation of photonic crystals. Introducing a new catalyst when outstanding materials are already occupying the scene is never an easy task, yet, this was attempted with nickel oxide supported on Zr-doped mesoporous silica for the reduction of nitric oxide with ammonia (E. Rodríguez-Castellón, see p. 3331). Although the nature of the active Ni species is still unclear, this new catalyst has definite advantages due to its improved activity at low temperature. Identifying the nature of the active species during catalytic operation in *realistic* conditions was demonstrated using so-called "*operando*" Raman spectroscopy (M. A. Bañares, see p. 3337). With an optically transparent quartz reactor, laser light becomes a powerful probe of the surface species, however harsh the reaction conditions are. Convincing evidence was presented that this vibrational spectroscopy is able to identify the surface groups on supported vanadium oxide catalysts during the oxidative dehydrogenation of propane. The last paper (J. D. F. Ramsay, see p. 3343) revisited the presentation by Prof. Pinnavaia, showing the extent of interest in zeolite colloidal precursors. In this case, a new two-step preparation method for microporous zeolitic membranes was proposed, again using the trick of first preparing colloidal seeds. These quasi-amorphous colloidal particles are then deposited on a substrate and allowed to grow and to crystallise further until the inter-crystallite voids close. The membranes obtained should be effective gas separators able to operate under harsh conditions. The discussion centred on the practical impediments to membrane preparation including points such as choice of appropriate supports, homogeneous growth of the zeolite phases and cracking of the active thin layer of the membranes. Also of note is the extensive use and utility of *in situ* small angle scattering methods, both neutron and X-ray, in this work.

In summary, the plenary lecture, the keynote lectures, the discussion papers and the poster presentations stimulated fruitful discussions on chemistry related to materials within a field of growing impact. The significance of porous solids and related materials is highlighted by the fact that approximately eight percent of the GNP in developed countries is devoted their use in such crucial applications as the purification of air and water, and also to energy and environmental management, including fuel generation, green chemistry processes and electrical energy storage. In addition, structural materials based on nanocomposites, including layered and modified porous substrates, were identified as important emerging areas of application. Advanced functional materials showing a variety of optical, magnetic and electrical properties were discussed during MD5, illustrating the broadness of incidence of this class of materials.

Finally, we would like to acknowledge to Prof. A. R. West for encouraging us to organise MD5 and for his continued support. We thank all of the members of the organising committee and, particularly, Christine Hall, Ian Farrell, Nicole Morgan, Karsten Harlow, Nichole Gibson and Graham McCann from the RSC staff for their continuous assistance with and management of the MD5 meeting and its publication. We would also like to thank the delegates for their active participation and for entering into the spirit of the Materials Discussions meetings. Our sincere gratitude goes to the Session Chairs for their excellent leadership of the discussions, and also for highlighting their sessions and helping with the writing of this preface.

Eduardo Ruiz-Hitzky
Pilar Aranda
Instituto de Ciencia de Materiales de Madrid
CSIC, Spain