Supramolecular Host-Guest Systems in Zeolites Prepared by Ship-in-a-Bottle Synthesis

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Zeolites have a microporous system defining large cavities interconnected by smaller windows. These cages can accommodate large molecules whose size, however, can be too big to cross the windows. The most important examples of these tridirectional zeolites are faujasites X and Y, but examples of other suitable zeolites are Beta, EMT and MCM-22. The inclusion of large guests inside the cavities starts from smaller precursors that can diffuse through the zeolite pores and then react inside the cavities to form the target guest. This microreview discusses the special characterisation techniques necessary to study these systems, differentiating those that serve to assess the identity and purity of the guests from those that address the internal vs. external location of the guests with respect to the zeolite host. It is organized by grouping the examples of ship-in-a-bottle synthesis according to the potential application of the system as catalysts, photocatalysts, sensors, in molecular machines, etc. Although proper credit is given to the pioneering reports on ship-in-a-bottle synthesis, the emphasis is placed on the most recent examples of the literature covering up to mid 2003.
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A. General Aspects

1. Introduction

Zeolites owe their importance to their use as catalysts in gas-phase, large-scale petrochemical processes such as catalytic cracking, Friedel−Crafts alkylation and alkylaromatic isomerisation or disproportionation.[1−6] Zeolites are easy to separate from the reaction products, thereby offering convenient reactor design and allowing continuous-flow operation. Because they are thermally stable and chemically robust, zeolites can be almost completely regenerated by calcination in air when they become deactivated by the presence of large organic products that remain adsorbed.

The promising results of gas-phase reactions in zeolites have triggered an intense research effort aimed at

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Hermenegildo García (Herme) was born in Canals (Spain) in June of 1957 and studied chemistry at the Faculty of Science of the Universidad de Valencia (Spain) where he graduated in 1979 with Honors. He did his PhD on preparative organic photochemistry under the guidance of Prof. Miguel A. Miranda and this was awarded, also with Honors by the Universidad de Valencia in 1983. Then, he moved to the Technical University of Valencia where he initiated his career in 1983 first as Assistant Professor, becoming finally Full Professor in 1996. In 1991 he was appointed member of the Institute of Chemical Technology, a joint centre depending on the Spanish National Research Council (CSIC) and the Technical University of Valencia that was founded in that year. He stayed as a postdoc at the Chemistry Department of the University of Reading (U.K.) with Prof. Andrew Gilbert in 1987, and later took three periods of sabbatical leave in 1992−1993 (one year), 1995 (six months) and 2000 (three months) at the University of Ottawa joining the Laser Flash Photolysis group led by Prof. J. C. (Tito) Scaiano. He has co-authored over 200 papers most of them dealing with the application of zeolites as hosts of organic guests and as solid catalysts. He holds three international patents. His main current interests are in supramolecular photochemistry and photocatalysis, the development of photoactive nanoscopic materials and heterogeneous catalysis.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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developing the potential of zeolites as acid-base and redox catalysts for the production of chemicals and fine chemicals.[7,8] As a result of these studies, heterogeneous catalysis of organic reactions by zeolites can be considered a mature field, and the industrial applications of zeolites for membranes, adsorption-separation and in the production of fine and specialty chemicals are expected to grow in the near future.

In addition to the current importance of zeolites in heterogeneous catalysis, it is likely that these solids will also attract interest in materials science for the development of functional materials, and in nanotechnology.[9] For these applications, zeolites provide a rigid matrix in which some active component or components can be included. Enantioselective catalysis, sensors, solid lasers, intelligent switches, membranes, waveguides and solar cells are emerging fields in which zeolites can be applied. The main problem to be solved for the application in nanotechnology is the preparation of submillimeter films in which the pores are oriented with respect to the substrate. Progress on film preparation has been made by "in situ" crystallisation of gels or the covalent attachment of zeolite particles to the substrate.[10−13]

A system that has vast potential for application in catalysis as well as for nanotechnology is that in which a functional guest is incarcerated inside the zeolite supercages without the possibility of diffusing out of the particle. In the field of catalysis, there are a number of reviews summarising the use of encapsulated coordination complexes as oxidation catalysts[14,15] and the possible strategies for the preparation of zeolite ship-in-a-bottle complexes, including the use of flexible ligands and zeolite synthesis around the complexes.[16] The generation of organic carbocations entrapped within the zeolite during a chemical reaction in the liquid phase has also been reviewed.[17] Considering the zeolites as catalysts, these carbocations are generally undesired species that poison and block the catalytic site, but in other cases their preparation has been purposely achieved.[17−19] This microreview focuses on the preparation, characterisation and properties of such supramolecular guest-zeolite materials, with special emphasis on their applications. Firstly, we will comment briefly on the main characteristics of zeolites as hosts. Then, we will describe adsorption procedures and the ship-in-a-bottle synthesis. We will cover characterisation techniques of encapsulated guests and how to address the internal vs. external location of the guest. The main body of the microreview describes the examples reported of ship-in-a-bottle synthesis. We have classified them according to the potential application that these host-guest systems can have.

2. Zeolites: Composition and Chemical Structure

Zeolites are crystalline aluminosilicates whose structure is formed by an array of corner-sharing SiO_4^{4-} or AlO_4^{5-} tetrahedra.[20−22] These building blocks become arranged in a periodic way to form channels and cages on a nano- and subnanometer scale of strictly regular dimensions, named micropores. The pores of the zeolites are open to the exterior and to the surrounding medium, thus allowing diffusion of molecules from the exterior to the interior of the zeolite particle. The existence of these accessible micropores ranks zeolites at the top of the list of solids exhibiting large specific surface areas, typically above 300 $m^2 \cdot g^{-1}$ with an internal void volume above 0.1 $cm^3 \cdot g^{-1}$.

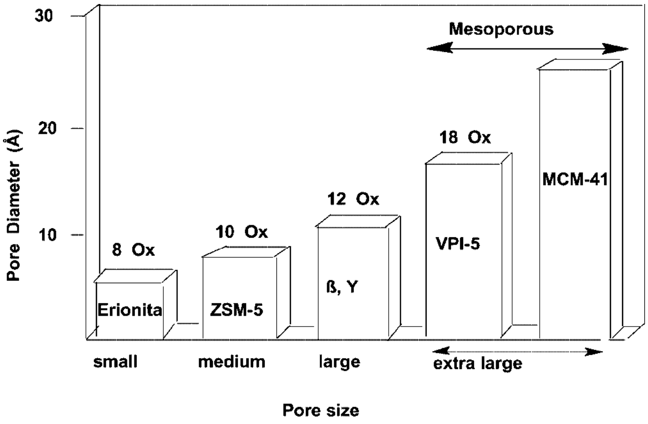
A zeolite framework containing exclusively oxygen-sharing SiO_4^{4-} tetrahedra is neutral. Al is a near neighbour of Si in the periodic table, both elements having similar ionic radii. When an Al atom replaces an Si atom isomorphically in the framework, this becomes negatively charged, one negative charge being introduced by each AlO_4^{5-} tetrahedron. The overall negative charge of these aluminosilicates requires the presence of organic or inorganic cations to maintain the electroneutrality of the solid.

Although there are natural zeolites, most of the over 100 zeolites known are synthetic. The first synthesis of zeolite Y by Barrer in the mid 1950s was an attempt to mimic the conditions under which natural zeolites were supposed to have formed on the Earth.[23−32] This synthesis has been widely recognized as one of the most important advances in the chemistry of the last century. Zeolites are obtained in the laboratory by crystallisation (either static or under continuous agitation) of gels containing alumina and silica in an aqueous medium at temperatures in the range of 100−190 °C and autogenous pressure, for several days or weeks.[33] Besides silica and alumina, the gel can be prepared from other sources of Al, Si and some other metals, and it may also contain quaternary ammonium cations to direct the crystallisation of a given crystal structure.

Zeolites are classified based on the symmetry of their unit cell, each structure being denoted by three capital letters.[34] An alternative classification that is more convenient here is according to the dimensions of the micropores (Scheme 1). In this regard the zeolites can be classified as having a small, medium or large pore size depending on whether the number of oxygen atoms and Si plus Al atoms is 8, 10 or 12, respectively.[35] The number of oxygen atoms defining the minimum ring of a pore determines roughly the dimension of the pores, which are approximately 3, 5 and 7 Å for the small-, medium- and large-pore zeolites, respectively. Recently, new structures containing pores of different dimensions have been reported.[36−39]

There has been an intense search for extra-large-pore zeolites (those having pores with more than 12-membered rings), but the success has been limited in the sense that, although some extra-large-pore zeolites or zeotypes have been synthesised, the resulting pores are not spherical and the minimum axis and structure are not much different from those of large-pore zeolites.[40,41]

Another aspect of importance regarding the micropore system of zeolites is the geometry of the pores. In this regard zeolites can be classified as uni-, bi- and tridirectional zeolites, depending on whether the channel system is arranged along one, two or the three Cartesian axes. The directionality of the zeolite pore system is relevant with respect to the ability of zeolites to include guests inside the micropores. Diffusion coefficients in unidirectional zeolites



Scheme 1

are typically smaller than those of tridirectional zeolites, which contain a much more open pore system.[42]

The phenomenon of inclusion of a molecule inside the rigid pores defined by the zeolite framework is commonly denoted with terms like adsorption, incorporation, inclusion or encapsulation. The latter three terms are used when the residence time inside the pores is indefinitely long, while in catalysis in which the access of the reagents and substrates to the internal sites is a necessary step in the mechanism and the products have to migrate away from the sites, the terms adsorption and desorption are the preferred ones.

The ability of zeolites to include organic or inorganic guests in their interior gives rise to a supramolecular chemistry in which the properties of the guest-zeolite assembly differs from the molecular properties of the guest in solution.[43] The control of the molecular properties by the zeolite may arise basically by the combination of any of at least five main factors including: (i) restriction of the mobility and conformational flexibility of the guest; (ii) shape-selectivity effects in which the molecular size of the reactants, transition states and products relative to the dimensions of the pores play a decisive role; (iii) compartmentalisation of the reaction cavity favouring geminate recombination and disfavouring escape effects; (iv) polarity of the zeolite internal voids promoting and stabilizing charged species; and (v) the presence of cooperating active sites in close proximity to the encapsulated species. Here we will provide examples that illustrate how incorporation into a zeolite can alter the *intrinsic molecular properties* of the included guest.

Different terms have been coined to refer to the zeolite adsorption-encapsulation chemistry. For instance, zeolites were initially defined by Barrer as molecular sieves to denote that certain molecules can access the interior of the pores, while others are too large and are size-excluded from the interior, the zeolites behaving as sieves of molecular dimensions.[20] In fact, zeolites commercially available from Aldrich are still indicated in the catalogue as molecular sieves instead of the three-letter code applied by the International Zeolite Association to classify any zeolite. Kochi coined the term *molecular pocket* to describe the effective protection of reactive guests occurring by encapsulation inside the rigid matrix defined by zeolite inert crystal structure.[44] The most general descriptor, *reaction cavity*, refers to the importance of certain properties of the environment surrounding reacting molecules such as flexibility and deformability, dimensions, and polarity among others.[45]

3. Adsorption Procedures

Guests can gain access to the interior of the zeolite particles through the micropores following different adsorption protocols which depend on the Coulombic charge of the guest, its diffusion coefficient, its stability and persistence. The simplest adsorption procedure for neutral guests that can diffuse into the pores consists of dissolving them in an inert solvent, preferably apolar, and placing the solution in contact with thermally dehydrated zeolite samples. Adsorption can be carried out by stirring the solid in the solution at room temperature or by heating. Due to the activation energy for diffusion within the micropores, mild heating can have a very large effect facilitating the adsorption.

It has to be remarked that the pores of hydrophilic zeolites are filled by co-adsorbed water, and this water has to be desorbed before proceeding to the inclusion of any guest. Typically, co-adsorbed water can be evacuated by heating the zeolite at temperatures above 100 °C under reduced pressure or by heating at higher temperatures under atmospheric pressure. After dehydration, water can be regained partially or completely very quickly upon exposure to the ambient moisture.

For guest adsorption from solutions, the nature of the solvent has a large influence. This effect is generally rationalised in terms of competition between guest or solvent adsorption. If a solvent is strongly adsorbed within the zeolite then the co-adsorption of the guest is impeded. On the other hand, if the interaction of the solvent and the zeolite is weak then solute adsorption is favoured. The interaction of the zeolite with solvents and simple guests can be discussed quantitatively by means of calorimetry, measuring the specific heat of adsorption. In the case of polar zeolites, it can be said that, in general, apolar, aprotic solvents promote adsorption of larger amounts of the guests than protic solvents.

Incorporation of guests inside the zeolite micropores can also be accomplished in the gas phase in those cases where the vapour pressure of the guests is sufficiently high at room temperature or when the substrate to be adsorbed can be heated to appropriate temperatures. Chemical vapour deposition chambers can be used for this purpose. The absence of solvent in vapour-phase adsorption facilitates the inclusion of the guest and, in addition, the resulting samples are free of contamination from adventitious presence of residual solvent molecules.

For cationic compounds, incorporation of the cation requires the exchange with the charge-balancing cation. This is easily done when the counterbalance cation is an alkali or alkaline earth cation. The ion exchange is normally carried out in water as solvent. A single ion exchange normally leads to partial cation replacement, the percentage of ex-

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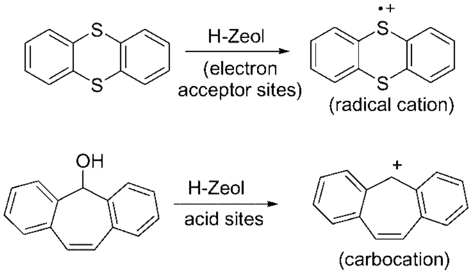
change depending on the initial solution concentration. The ion exchange is usually repeated two or three times increasing the initial solution concentration of the cationic guest to achieve a high level of ion exchange. Given that there are different positions where the charge-balancing cations can be located with respect to the zeolite framework, it can occur that, depending on the relative size of the cation being introduced with respect to the existing one, normally Na^+ or another alkali metal ion, not all the families of pre-existing cations can be exchanged. A prototypical case are faujasites in which the type-I and -II cations located inside the sodalite cages or hexagonal prisms are difficult to exchange.[20−22]

4. Ship-in-a-Bottle Synthesis

Besides incorporation of a guest from the exterior into the interior of the zeolite particle, a particular case is the in situ formation of species by adsorbing suitable precursors that will be transformed into the final guest. The zeolite may play an active role in the generation of the species by containing active sites that would interact with the guest precursor, promoting the transformation. Typically, the zeolite can have acidic or basic sites, but metallic centres can also be present. The type of transformations used to generate a trapped species can be elimination, substitution or a redox process. An example of the above reactions is the generation of organic radical cations by adsorbing the neutral precursor and abstracting a single electron. Another example is the generation of a carbocation by protonation and dehydration of an alcohol (Scheme 2).



Scheme 2

In most cases in which an immediate precursor is adsorbed, this compound contains most of the bonds of the final species and there is not a large difference in the size of the precursor and the final species. However, in some cases the final species that is formed in the zeolite arises from the coupling of several precursors and there is a notable increase in the number of atoms and size of the final guest.

For this situation and using tridirectional zeolites as hosts a possibility can be envisioned in which, due to the large molecular size of the resulting guest, it remains imprisoned inside the zeolite structure after its synthesis with an impeded diffusion. The internal voids of tridirectional zeolites have a geometry encompassing large cavities interconnected only by smaller windows. The most frequent cases are faujasites X and Y, whose internal voids are formed by almost spherical cavities of 13 Å diameter, called supercages, tetrahedrally interconnected through 12-membered-ring windows of only 7.4 Å diameter. Also, zeolite Beta has oval cages (7.4 × 11 Å) defined by the crossing of two perpendicular 12-membered-ring channels (ca. 7.4 Å) whose axes are slightly shifted. For these topologies, a situation can occur in which a guest has a molecular size that, on one hand, allows it to be accommodated inside the cages but, on the other, is too big to cross the smaller cavity windows. These guests will remain immobilized by the rigid zeolite framework but they can still interact with small substrates able to diffuse through the micropores.

The term ship-in-a-bottle was most probably coined by Herron, whilst working at the R&D centre of Dupont at Wilmington, who reported the synthesis of several types of metallic complexes encapsulated within zeolites.[46] The term ship-in-a-bottle alludes to the similarity of the resulting complex imprisoned within the zeolite framework with the artistic bottles containing a ship larger than the bottle neck. However, even before this term was coined other researchers had most probably already used this methodology. Thus, as an example, Romanovskii, publishing in Russian[47−49] and Schulz-Ekloff[50,51] independently synthesised metallic phthalocyanines inside faujasite X by treating *o*-phthalodinitrile with a transition-metal-exchanged faujasite at temperatures above 200 °C, a reaction that is archetypical of a ship-in-a-bottle synthesis.

Normally, the reactions employed in a ship-in-a-bottle synthesis also work well in solution. In those cases in which a homogeneous catalyst is needed in solution, the ship-in-a-bottle synthesis requires the presence of active sites in the micropores of the zeolites. These sites can be acidic, basic or metal atoms. Reactions suitable for a ship-in-a-bottle synthesis should start from precursors of suitable size and should give high product yields, or the by-products should be small enough to be separated by solid-liquid extraction. In fact, the only purification treatment applicable to the ship-in-a-bottle synthesis is solid-liquid extraction as this treatment is based on the desorption of starting material and by-products.

An alternative and complementary procedure to the ship-in-a-bottle synthesis is to build the bottle around the ship. This consists in performing the crystallisation of the zeolite from a gel that contains the preformed guest. Two obvious limitations of this methodology is that the guest has to survive the relatively harsh conditions of the zeolite synthesis in terms of pH and temperatures for long periods, and the zeolite crystal structure should still be formed in the presence of the guest. The ease of crystallisation explains why the build-the-bottle-around-the-ship approach has been employed almost exclusively for faujasites X and Y.

An approach worthy of being explored more systematically would be exactly the reverse of a ship-in-a-bottle synthesis, the target being the synthesis of new zeolite structures by using large guests molecules that could act, in principle, as templates or structure-directing agents for the crystallisation of the aluminosilicate. A precedent of this is the synthesis of extra-large-pore UTD-10 using a Co^{II} complex of 1,8-bis(trimethylammonio)-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane reported by Balkus, Jr.[16,52]

After a successful ship-in-a-bottle synthesis the main feature of the resulting zeolite containing a big organic guest inside the cavities is that the guest becomes immobilized and imprisoned inside the cages without the possibility of diffusing out of the particle. In the field of supramolecular chemistry of rotaxanes and catenanes, Stoddart has coined the term "mechanical immobilisation" to describe a situation in which one of the components of a supramolecular assembly cannot diffuse independently from the other and both of which are held in place by physical forces without the existence of a covalent bond between them.[53,54] According to this definition, the same term will apply to the system comprising a big guest encapsulated within a tridirectional zeolite since, despite the fact that there is no covalent bond connecting both entities, the guest remains entrapped, without the possibility of escape, due to physical (forbidden van der Waals atomic overlapping) forces.

Also useful when dealing with ship-in-a-bottle synthesis is Turro's "@" notation used to indicate that the guest is assumed to be located inside the particle and not exclusively or predominantly on the external surface.[55]

5. Characterisation Techniques

When performing a ship-in-a-bottle synthesis there are two crucial issues that need to be addressed independently. These two questions are the identity and purity of the encapsulated species and the location of the guests with respect to the zeolite particle.

The techniques to study the nature of the guest differ if we are dealing with a completely inorganic guest, such as metal clusters, or an organic species. In the case of purely inorganic guests X-ray diffraction, EXAFS, XANES and electron microscopy are the most important tools, together with some particular techniques such as diffuse reflectance UV/Vis, Raman and Mössbauer spectroscopy. The dispersion and size distribution of the clusters for heavy atoms can be determined by X-ray diffraction and can also be observed by electron-microscopic techniques. Even UV/Vis spectroscopy can be useful for this purpose since some typical inorganic clusters absorb visible light, the λ_{max} of the band being related to the average cluster size. IR and Raman spectroscopy on the other hand can also provide some information about the nature of the guest and, by means of probe molecules, can indirectly report on the ability of the clusters to interact with adsorbates. CO, NH_3 and pyridine are among the favourite probe molecules for Lewis-acid clusters.[56]

Spectroscopy,[57] including UV/Vis,[58] IR,[59−61] Raman[62] and multinuclear solid-state NMR,[63] is also one of the favourite techniques to determine the nature of metallic complexes or organic guests incorporated inside the zeolite pores.[64] It is worth noting that in these techniques either the zeolite framework does not give any signal or, in the worst case, at only certain spectral wavelengths. For instance, zeolites composed of silicon and not containing any other heteroatom are transparent in the UV/Vis spectrum at wavelengths longer than 220 nm. It has been reported that highly pure zeolites absorb exclusively in the vacuum UV region ($\lambda < 200$ nm). Since UV/Vis radiation penetrates deep inside the zeolite particle, it is possible to record the optical spectrum of a guest that is occluded inside the zeolite grain without interference of the zeolite framework, in a similar way as the optical spectra of organic guests are recorded in other matrices. Perhaps the major peculiarity is that diffuse reflectance techniques,[65] rather than the transmission techniques typically used for solutions, are used to record the UV/Vis spectrum.

Also, in IR spectroscopy zeolites are transparent at most IR wavelengths and, importantly, in the 3400−1300 cm^{-1} zone characteristic of the principal organic functional groups.[60] Zeolites possess a strong absorption due to the T−O bonds at around 1000 cm^{-1}, accompanied by weaker framework O−H stretching bands in the 3700−3500 cm^{-1} zone. Apart from these localised regions, the zeolite framework does not interfere in the IR absorption of the incorporated guests.

Solid-state ^{13}C NMR spectroscopy can also be used for identification purposes.[63] However, the low sensitivity of this technique makes it not very useful unless isotopically ^{13}C-labelled compounds are used or the guest loading is sufficiently high. Other nuclei such as ^{19}F, ^{29}Si, ^{31}P, etc. can be important in some particular cases.

One of the most useful approaches to determine the nature of the species resulting after the ship-in-a-bottle synthesis is to compare the reported spectroscopic properties of a species in solution with that recorded for the zeolite sample. Caution should be exercised when comparing the spectra, since some other species or by-products may have also similar properties. Particularly important as identity criteria are IR and Raman spectra taken as fingerprints due to the large number of peaks with various intensities appearing in these spectra. However, there are some cases in which the spectra of the species in other media are not available or the spectroscopic features are too general to be attributed unambiguously to a single species. One common reason for this is the instability of the species in other media. In these cases, or in general as a complementary strategy to the analysis of the spectroscopic data, one approach to determine the nature of the incorporated guest consists in dissolving the zeolite framework with concentrated hydrofluoric acid or with a mixture of HF and HNO_3 and extract the guest or the products derived from it that can thus be analysed. The limitation of this approach is the instability of the guest to this aggressive treatment. However, it is worth mentioning that some organic groups can survive HF treatment and, when this occurs, the method becomes useful. On the other hand, given the large amount of inorganic salts present in the liquor resulting after dissolving the zeolite, extraction of the guest from these solutions is problematic. High loading and low polarity of the guest facilitates the extraction.

A good practice when performing the ship-in-a-bottle synthesis is to analyse the extractable products. In principle, it is logical to assume that the products observed in solution, if bulky enough, will also be trapped inside the zeolite pores since it is expected that it will be formed equally outside and inside the zeolite grain. If, on the other hand, the recoverable products are not bulky enough to remain entrapped inside the zeolite, they can give a useful information on the operating reaction mechanism and their formation has to be compatible with the overall reaction scheme.

6. Evidence to Support the Internal Location of Encapsulated Guests

Once the nature of the species is known, a different question that requires specific techniques to be answered is the location (internal vs. external) of the guests. The fact that a synthesis has succeeded does not guarantee that the guest is located predominantly in the interior of the grains. In fact it would be reasonable to assume that during the synthesis a distribution of guests between the external surface and the internal pores occurs. Since the total surface area in a zeolite is predominantly internal (over one order of magnitude larger than the external surface), it is logical to consider that most of the guests are located internally, particularly when dealing with high loading samples.

However, ship-in-a-bottle syntheses conducted using amorphous silicas have demonstrated in some cases that the product can also be formed on these non-porous solids. Likewise, in the case of small- or medium-pore-size zeolites in which large guests cannot be accommodated within the interior of the micropores, the synthesis can also succeed. For these solids (either non-porous or small-pore-size zeolites) there is no doubt that the product formed has to be located exclusively on the external surface. Therefore, the formation of the product (as assessed by spectroscopic means) in a tridirectional zeolite can never be taken as evidence per se of its location.

Direct evidence of the internal location of guests can be obtained when the guests are heavy metal atoms by means of high-resolution X-ray diffraction, neutron scattering or high-resolution transmission electron microscopy. These techniques have been applied in fact to the study of zeolites devoid of any guest to address the crystallographic position of the charge-balancing cations. However, organic compounds do not normally give a clear signal or image with these techniques due to the low atomic weight of carbon. Nevertheless Baerlocher et al. have reported direct evidence of organic guest location by high-resolution X-ray diffraction.[66] Thus, the location of organic guests has to be addressed indirectly and generally by a combination of several techniques since each of them have serious limitations that can induce errors if no special precautions are taken.

It is frequently assumed that exhaustive solid-liquid extraction can be a proof of the internal location of bulky guests. Molecules small enough to diffuse through the internal pores should be recoverable by solid-liquid extraction even if they are adsorbed internally. However, this assumption has to be proved and supported by appropriate blank controls. Thus, known amounts of a compound can be adsorbed on a zeolite and then extracted to determine the efficiency of the extraction protocol. On the other hand, large guests supported on amorphous silicas can also be submitted to solid-liquid extraction to determine the efficiency of the recovery when these guests are deposited on the external surface. In any case, it can be stated that, although exhaustive solid-liquid extractions are a necessary workup in a ship-in-a-bottle synthesis, the fact that the zeolite still contains some guest after this treatment is only a weak indication of its internal location, particularly for low residual loading of the guest.

An indirect technique used to address the location of a guest in a zeolite is isothermal gas adsorption. Surface area and pore volume measurements should reflect a decrease in the specific values due to the presence of the guest occupying the internal void. However, in order to provide meaningful data isothermal gas adsorption requires prior evacuation of co-adsorbed water by thermal desorption under reduced pressure. Thermal treatment must be then carefully performed since mild desorption conditions could still leave some residual water adsorbed on strong sites and a more severe treatment may lead to the decomposition of the organic guest. Since most organic compounds start to degrade at temperatures above 300 °C, this is approximately the common limit for pre-treatment of these surface area measurements. For certain zeolites, particularly those having strongly acidic sites, 300 °C may not be sufficient to desorb all the adsorbed water completely and the porosity measurements will therefore be disguised. On the other hand, a labile organic guest may not resist prolonged heating at high temperature.

XPS provides an elemental analysis of a shallow layer (approx. 20 nm depth for soft X-rays) of the zeolite grain. XPS analysis can be quantitative by integrating the area of the peak corresponding to each element and calibrating the response of each atom using standards. A technique that is used in materials science to determine the depth of a metal corrosion is to combine XPS analysis and fast atom bombardment that produces the disappearance and ablation of the outermost layer exposed to the high-energy sputtering. The Ar^+ ion can be used for this purpose. If the combination of XPS and Ar^+ ion sputtering is applied to zeolites, a map of the elemental composition vs. the time of exposure to the Ar^+ beam is obtained. The time of the Ar^+ sputtering can be related to the depth of penetration from the external surface to the interior of the zeolite particle due to the destruction and evacuation of the exposed zeolite framework. Therefore, a plot of the percentage of a given element vs. penetration depth can be obtained. If the percentage of C atoms with respect to the total of other atoms (O + Si + Al) increases along the distance from the particle surface, this can indicate that the guest is located predominantly in the interior of the grains. Figure 1 shows a reported example of the use of XPS/sputtering for the purpose of mapping out the C composition along the particle radius.

The limitation of the XPS combined with fast atom sputtering technique may arise from the texture and mor-

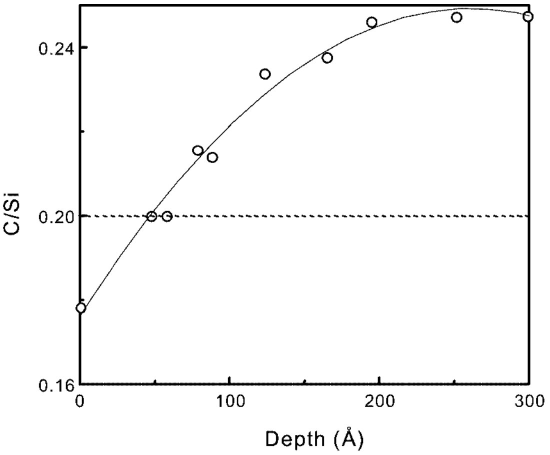


Figure 1. XPS analysis of the atomic C/Si ratio along the depth of penetration on a zeolite particle containing tris(4-methoxyphenyl)methyl cation (taken from ref.[67]; reprinted with permission; © 1996 American Chemical Society)

phology of the zeolite samples. While for continuous and flat surfaces, such as those of metals, the above technique really provides a map of the composition along the penetration in the material, when working with powders composed of individual particles of micrometer size the situation is more complicated. Depending on the sample preparation and how the powder is presented, the differences in the composition along the time of sputtering may not really reflect differences along the zeolite particle depth, but rather differences from particle to particle. Differences in the packing of the particles, sedimentation and other aspects related to the agglomeration of a multitude of particles, rather than penetration inside an individual zeolite particle, can also be responsible for differences in the XPS upon Ar^+ sputtering.

For many zeolites, the location of charge-balancing cations in as-synthesised, highly crystalline samples has been conclusively demonstrated by high-resolution X-ray diffraction and neutron scattering. If a guest is replacing a significant fraction of these structural cations, it can be assumed that they will occupy the initial positions of the original cations. Even if the crystallographic positions are not exactly the same for the initial cation and the replacing guest, it is reasonable to assume that the positions have to be as close as possible in order to minimize the electrostatic energy. Thus, if a large fraction of a cation located internally is replaced by a bulky guest, the guest has to be also within the micropores.

A related case is that of protonic zeolites having acidic hydroxy $\equiv Si-(OH)-Al\equiv$ bridges. In IR spectroscopy, different framework hydroxy groups may exhibit different absorptions. In particular, for fully protonic HY zeolite there are distinctive IR hydroxy bands related to external silanols (3740 cm^{-1}), acidic bridged OH inside the sodalite cage (3670 cm^{-1}), OH in the supercage (3650 cm^{-1}), and OH in the sodalite hexagonal prisms (ca. 3550 cm^{-1}).[56] These peaks appear as sharp absorption bands in the spectra of dehydrated HY samples, and some other OH groups can also be present depending on the type of sample and the presence or not of non-framework Al. If as a result of a ship-in-a-bottle synthesis a bulky guest is located in the Y supercage replacing these protons totally or partially, then quantification of the peak corresponding to the vibration of this type of hydroxy groups in the IR spectra for exactly the same weight of the zeolite before and after the ship-in-a-bottle synthesis should reflect the decrease in the population of these acidic OH groups. Since the location of these groups is known, their replacement requires that the formed guest occupies a position close to the original OH.

However, also in this case there are some artifacts that can influence the intensity of the OH groups without being actually replaced. Since these OH groups are acidic, the presence of residual amounts of solvents, reactant, or byproducts may broaden the acidic OH peak considerably, giving the impression that its intensity has decreased or making the peak integration inexact. In order for these measurements to be valid, the spectrum of the sample after the ship-in-a-bottle synthesis has to be recorded under conditions in which nothing alters the OH groups. Blank controls in which a zeolite sample is submitted to an analogous ship-in-a-bottle treatment but without a necessary reagent to form the entrapped guest is also a good practice to compare the IR spectra with and without guest.

B. Applications of Zeolite-Embedded Guest Systems Obtained by Ship-in-a-Bottle Synthesis

1. Ship-in-a-Bottle Systems as "Zeozymes"

There are some enzymes in which a metallic complex is embedded with the tridimensional structure of a protein. The metallic complex acts as the catalytic site while the access of the substrate to the site is controlled by the surrounding protein skeleton. Other properties such as solubility and the micropolarity of the environment site isolation are also determined by the protein. Inspired by the enzyme constitution, it is possible to imagine an analogous system comprising a catalytically active metallic complex but embedded within an inorganic matrix. The term "zeozyme" was constructed by the combination of the words *zeolite* and *enzyme* and refers to the latter possibility.[15,68,69] There is no doubt that this application of ship-in-a-bottle synthesis will attract a renewed interest in coming years motivated by the understanding of new enzymatic systems.

In this context, probably the first example of a synthesis termed as a ship-in-a-bottle synthesis was a $Co^{II}-$salen complex that was prepared by adsorbing the flexible salen ligand into a Co^{II}-ion-exchanged zeolite.[46]

Transition metal complexes of salen are widely used as catalysts in homogeneous solution for a large number of reactions such as epoxidation of alkenes, epoxide ring aperture, nucleophilic additions to carbonyl and imine groups, CO_2 fixation, etc.[70−74] The term *salen* for the ligand is the acronym standing for bis(salicylidene)ethylenediamine. These salen complexes are a particular case of Schiff-base

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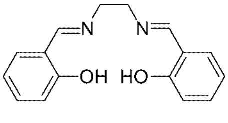
complexes, since one of the coordination bonds between the metal atom and the ligand occurs through the imine group that is known in organic chemistry as the Schiff base.



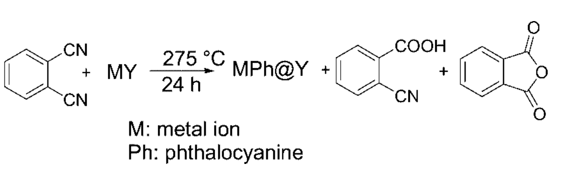
salen

In contrast to the flexibility of the salen ligand (particularly through the ethylene bridge), the resulting metal complex is rigid and becomes entrapped inside the zeolite cavities.[46] Encapsulated Co^{II}−salen complex shows affinity for O_2, forming a 1:1 adduct exhibiting a somewhat lower binding equilibrium than in solution, but an excellent resistance to undergo autooxidation even at elevated temperatures.[46] This system has a resemblance to that of hemoglobin, the Co^{II}−salen acting as a prosthetic group binding oxygen reversibly and the zeolite behaving as an "*inorganic*" protein. This example developed by *bioinspiration* is the origin of the word *zeozymes.*

Since Co^{II}−salen many other transition-metal−salen complexes, such as those of $V{=}O^{2+}$ [75] and iron,[76] have been reported. The influence of the preparation procedure and reaction temperature on the efficiency of the complex formation has been studied for Rh^{III}−salen encapsulated in zeolites X and Y.[77,78]

Jacobs has used a biomimetic approach to design encapsulated mono- and polynuclear iron catalysts with activity similar to *monooxygenase* metalloproteins that catalyse the incorporation of oxygen atoms from dioxygen into organic substrates.[79]

Metallophthalocyanines can also be entrapped inside faujasites X and Y by a ship-in-a-bottle synthesis starting from *o*-phthalodinitrile and the transition-metal-exchanged zeolite or by a build-the-bottle-around-the-ship strategy. Balkus, Jr. has made significant contributions in this area and has written several reviews on the preparation and catalytic activity of encapsulated metallophthalocyanines.[75,80] As mentioned earlier in the introductory sections, after the pioneer work of Romanovskii and Schulz-Ekloff, Herron coined the term ship-in-a-bottle synthesis and, as well as the first metallic complexes, he also prepared iron−phthalocyanine inside faujasites X and Y by thermal tetramerisation of *o*-phthalodinitrile templated by iron ions (Scheme 3).[81] His idea was to mimic the activity of cytochrome P 450, which is able to oxidize alkanes with molecular oxygen, but replacing the flexible, but labile protein surrounding the prosthetic iron centre by the rigid and robust zeolite framework.



Scheme 3

The molecular size of the flat, relaxed geometry of the phthalocyanine macrocycle (about 14 Å of diameter) is too large to be accommodated inside the supercages of faujasites, whose free volume is also a function of the nature of the charge-balancing cations occupying site-III positions in the supercage. Since it is a fact that the ship-in-a-bottle synthesis of phthalocyanines is feasible, it has been proposed that the heteroaromatic macrocycle adopts a roof-like, rather than a flat, conformation to fit inside the cavities. Figure 2 shows a molecular modelling of Cu^{II}−phthalocyanine inside an ideal all-silica faujasite. Furthermore, in an interesting report, the synthesis of much bulkier iron−tetra-*tert*-butylphthalocyanine (estimated diameter of 19 Å) has been successfully accomplished starting from pre-encapsulated $[HFe_3(CO)_{11}]$ iron−carbonyl clusters and 4-*tert*-butyldicyanobenzene inside NaY.[82] Based on the characterisation by EXAFS, Mössbauer, FT-IR and diffuse-reflectance UV/Vis spectroscopy, the authors propose that the tetra-*tert*-butylphthalocyanine is located inside the zeolite supercage in a conformation far from planar.[82] Due to the steric compression compared to the parent iron−phthalocyanine, the tetra-*tert*-butyl derivative exhibits higher activity and selectivity toward terminal hydroxylation of *n*-hexane and *trans*-epoxidation of stilbenes with PhIO. This higher regioselectivity indicates a preferential attack of oxygen in the active Fe=O species on the terminal carbon atoms of the substrate. It would be of interest to gain a deeper understanding of the conformation, strain and location of this very large phthalocyanine complex.

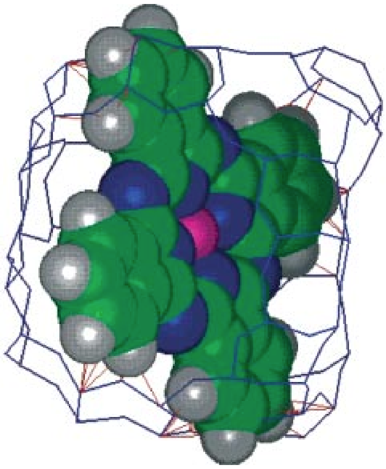
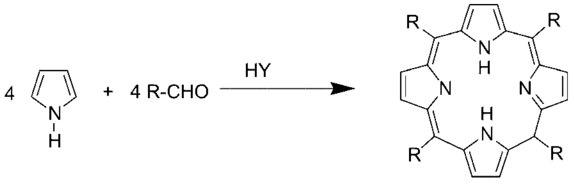


Figure 2. Molecular model showing copper−phthalocyanine encapsulated inside the supercage of zeolite Y (see also ref.[83])

An approach to avoid forcing the steric compression of phthalocyanine has been to use novel zeotypes with pore sizes larger than those of conventional faujasites. Co^{II}−phthalocyanine has been encapsulated in the large cavities of zeolite EMT at a loading of one complex for every six supercages.[84] The resulting Co−phthalocyanine@EMT exhibits a turnover number for the oxidation of ethylbenzene with molecular oxygen of about 22000. Likewise, Jacobs and co-workers have reported the encapsulation of iron−phthalocyanine inside large-pore-size VPI-5, which is a monodirectional aluminophosphate of extra-large pore size.[85−87] The VPI-5-occluded iron−phthalocyanine acts as a catalyst for alkane oxygenation using iodosobenzene. Jacobs has also reported an interesting further elaboration of the encapsulated phthalocyanine by preparing a composite in which the fibres of a partially crosslinked poly(dimethylsiloxane) polymer holds the zeolite containing the phthalocyanine complex.[88] This poly(dimethylsiloxane)/zeolite composite acts as a membrane at the interphase between aqueous hydrogen peroxide and hydrophobic cycloalkene and can promote the catalytic oxidation of alkenes, mimicking again the activity of cytochrome P 450.[88]

In an attempt to increase the stability and the turnover numbers of the encapsulated metallophthalocyanines, Balkus, Jr. described the synthesis of Ru^{II}−perchloro-[89] and -perfluorophthalocyanine[75,90−92] inside zeolite X. The methodology followed in this case was to build the bottle around the ship.[91] These perhalophthalocyanines show activity for the oxidation of cyclohexane with *tert*-butyl hydroperoxide and cyclohexene and stilbene with oxygen.[92] The perfluorinated phthalocyanine shows no signs of deactivation, in contrast to the nonfluorinated analogues.[91]

Related to encapsulated metallophthalocyanines are the attempts of ship-in-a-bottle synthesis of *meso*-tetrasubstituted porphyrins that formally possess the same aromatic macrocycle. This synthesis has been attempted by condensation of pyrrole with aldehydes (Scheme 4).[93] Although porphyrins are expected to be more flexible than phthalocyanines, and porphyrins are among the products observed in the solution during the ship-in-a-bottle synthesis, spectroscopic characterisation reveals that it is a precursor of the protoporphyrin type that is present inside the zeolite. It has been assumed that the lower thermodynamic stability of porphyrins as compared to phthalocyanines makes their ship-in-a-bottle synthesis unsuccessful, particularly the last oxidative aromatisation step that requires the achievement of planarity. In this context, and given the number of enzymes having metalloporphyrins and their interesting catalytic activity, it would be of interest for the development of the zeozyme concept to explore other zeolites with larger pores as hosts for porphyrins.



Scheme 4

There are metalloporphyrins, however, that can be encapsulated within faujasite by using the build-the-bottle-around-the-ship approach, crystallising the zeolite gel around the porphyrin. One example is the preparation of the metallotetrakis(*N*,*N*,*N*-trimethylanilinium)porphyrin cation entrapped in faujasite Y that was used as a catalyst for the oxidation of cyclohexene.[94] The latter strategy of crystallising the zeolite around the guest may work well for faujasites for which no structure-directing agent is required. In this case, the metallic complex has to be sufficiently robust to resist the hydrothermal zeolite crystallisation (typically above 100 °C and alkaline pH for at least a few hours) and has to have a relatively high solubility in water.

2. Ship-in-a-Bottle Systems as Catalysts

Moving further from the initial zeozyme concept to the broader use in catalysis, one general methodology to transform a successful homogeneous catalyst into a heterogeneous one consists in immobilizing it onto a large-surface-area support. Immobilisation of the homogeneous catalyst permits its recovery from the reaction mixture and its reuse in consecutive runs. Immobilisation also allows the design of continuous flow reactors in which the catalyst is in a different phase than the reactants and products. In this context, the ship-in-a-bottle methodology has been used since the early days to prepare efficient solid catalysts.

a. Hydrogenation

Carbonylmetal clusters have been synthesised in zeolites, and remain trapped in the cages, by the ship-in-a-bottle methodology.[95,96] Thus, neutral carbonyl clusters of Pd, Rh and Ir have been synthesised in the α cages of Y zeolite. The general procedure involves an ion-exchange process of amine complexes such as $[Pt(NH_3)_4]^{2+}$, $[Pd(NH_3)_4]^{2+}$, $[Rh(NH_3)_5Cl]^{2+}$, $[Ir(NH_3)_5Cl]^{2+}$, and even an $[Rh(H_2O)_6]^{3+}$ complex, with NaY zeolite, followed by calcination, reduction and CO treatment under different reaction conditions. In this way, the ship-in-a-bottle synthesis of $Pd_{13}(CO)_x$, $Rh_6(CO)_{16}$, and $Ir(CO)_3Cl$ has been successfully achieved.[97−100] When a more basic faujasite zeolite (NaX) is used, anionic carbonylmetal clusters of platinum $\{[Pt_{15}(CO)_{30}]^{2-}\}$, rhodium $\{[Rh_6(CO)_{15}]^{2-}\}$, and dimetallic Pt−Rh $\{[PtRh_5(CO)_{15}]^{-}\}$, and Fe−Rh $\{[Fe_2Rh_4(CO)_{16}]^{2-}\}$ can also be prepared inside the supercavities.[101−104]

Some mononuclear Ir species can migrate through the channels and cavities of the zeolites when heated. After CO treatment they give either neutral carbonyl clusters such as $[Ir_4(CO)_{12}]$ or $[Ir(CO)_{16}]$ when using zeolite NaY,[105−108] or anionic clusters when zeolite NaX is used.

Encapsulated metal−salen complexes have also been used as catalysts for reactions different from those catalysed by enzymes. Hölderich and co-workers have prepared Pd^{II}− and chiral Co^{II}−salen complexes encapsulated within zeolites and used them as carbonyl hydrogenation catalysts.[109] Encapsulated Pd^{II}−salen is able to promote the hydrogenation of methyl pyruvate with complete selectivity at conversions higher than 70% and that of methyl acetoacetate with a product selectivity of 92% at about 50% conversion, while bulkier substrates such as isopropyl and *tert*-butyl pyruvate gave less or no conversion.[109]

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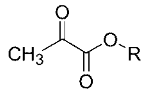
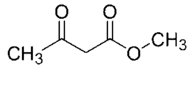
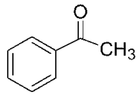


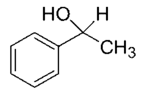
alkyl pyruvate



methyl acetoacetate



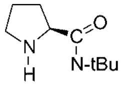
acetophenone



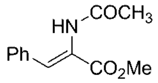
1-phenylethanol

In the case of the chiral Co^{II}−salen complex, although the selectivity for the conversion of acetophenone to 1-phenylethanol using the encapsulated Co complex was complete, the enantiomeric excesses at 25 °C were very low (8%) although higher than those of the homogeneous complex at lower temperatures (−10 °C). In agreement with the work on Mn^{III}−salen complexes, which will be mentioned shortly, the presence of large substituents on the ligand also precludes the ship-in-a-bottle synthesis of the Co complex and the resulting complex is located exclusively on the external surface, leading to enantiomeric excesses lower than those achieved with the same complex in homogeneous phase.[109]

Heterogeneous hydrogenation catalysts based on incarcerated metallic complexes other than salen have also been widely used. A complex of (cyclooctadiene)Rh^I and prolinamide or *N-tert*-butylprolinamide has been prepared inside zeolite, the resulting solids exhibiting a higher specific activity for the hydrogenation of alkenes than their homogeneous counterparts.[110] For the enantioselective hydrogenation of methyl (*Z*)-2-acetamido-3-phenylacrylate the enantiomeric excess was much higher with the heterogenized catalyst than with the homogeneous complex.



N-tert-butylprolinamide



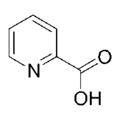
methyl (*Z*)-2-acetamido-3-phenylacrylate

b. Acid Catalysis

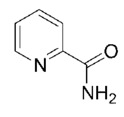
The heteropolyacid $H_3PW_{12}O_{40}$ is an almost spherical cluster of about 8 Å diameter. Its Keggin structure, with a central tetrahedral PO_4 core and internal tungsten atoms, makes this compound very rigid and undeformable preventing it from crossing the 7.4 Å windows of faujasites. One important property of phosphotungstic acid is its strong acidity, even higher than that exhibited by pure sulfuric acid due to the negative charge delocalisation through the outer oxygen layer of the structure. In spite of this superacidity, phosphotungstic acid has been synthesised inside the cavities of zeolite Y without destroying the crystal structure. ^{31}P MAS NMR spectroscopy shows a broad signal at $\delta = -14.4$ ppm that is assigned to the Keggin heteropolyacid interacting with the zeolite Al atoms. The encapsulated heteropolyacid exhibits high activity for *m*-xylene isomerisation and disproportionation.[111]

c. Oxidation Catalysis

Picolinic acid as a ligand for Fe^{III} was used successfully by Barton for the oxidation of cyclohexane by hydrogen peroxide.[112] Garcia and co-workers reported the encapsulation of iron picolinate inside a series of zeolites and found that the zeolites containing the encapsulated picolinate complex are efficient and reusable heterogeneous catalysts for the oxidation of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone.[113] Mordenite was found to be the best host for this purpose.[113] Analogously, vanadyl picolinate encapsulated within NaY is also active for the oxidation of alkanes, alcohols and benzene with hydrogen peroxide.[114,115] Jacobs has also reported the ship-in-a-bottle synthesis of an iron complex of a tetradentate N_4 ligand derived from 2-pyridinecarboxamide that is able to effect the oxidation of cyclohexane to cyclohexyl hydroperoxide as well as cyclohexanol and cyclohexanone.[116] In most of these iron oxidations it is widely assumed that the catalytically active species is a high-valent Fe^{IV}=O species.

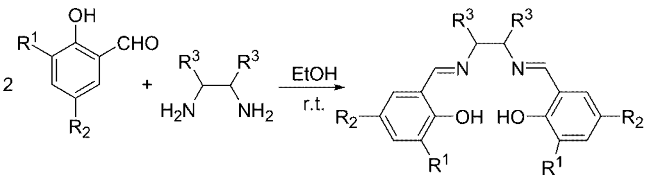


picolinic acid



2-pyridinecarboxamide

Many related ligands can be easily derived from salen by modifying the ethylenediamine bridge or by introducing substituents in the salicylidene aromatic moiety and they can be easily obtained by the condensation of a primary diamine with salicylaldehyde. This reaction is normally carried out by stirring an ethanolic solution of the salicylaldehyde and the diamine at room temperature until the product has formed (Scheme 5).



Scheme 5

Chiral salen ligands can be easily obtained if one uses a single enantiomer of a chiral diamine, as has been reported in solution. In fact the most important application of salen complexes is as asymmetric catalysts for the enantioselective epoxidation of alkenes using the manganese complex of bis(2,4-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine that is commonly known as the Katsuki−Jacobsen catalyst.[117,118]

In 1997, and almost simultaneously, two independent communications reported the ship-in-a-bottle synthesis of a chiral manganese Schiff-base complex inside faujasite and

EMT zeolites and used them as enantioselective catalysts for the heterogeneous epoxidation of alkenes.[119] (*Z*)-Methylstyrene and indene are two favourite substrates for the study of the enantioselectivity of asymmetric epoxidation. The enantiomeric excesses obtained with these zeolite-bound Mn^{III}−salen complexes were only modest (about 60%), particularly compared to the enantiomeric excesses that can be achieved in solution for the bis(2,4-di-*tert*-butylsalicylidene) derivative. It has to be noted, however, that due to steric restrictions the actual chiral salen ligand encapsulated within the Y zeolite cages lack the bulky *tert*-butyl substituents. Molecular modelling predicts that the tetra-*tert*-butyl-substituted salen ligand is too large to be accommodated inside the zeolite Y supercage. Figure 3 shows a visualisation of the Mn^{III}−salen complex obtained by freezing the geometry of zeolite Y devoid of framework Al to the crystallographic positions and optimising the geometry of the complex at the semiempirical MNDO level. A recent report, however, has challenged this modelling by claiming the preparation of the tetra-*tert*-butylsalen derivative inside the supercages of zeolite Y.[120] The authors have claimed to be able to prepare the encapsulated complex by adsorbing the preformed bulky ligand into the zeolite pores, something that molecular modelling predicts should not be possible. Recently, chiral vanadyl−di-*tert*-butylsalen complexes have been grafted in the walls of MCM-41.[121]

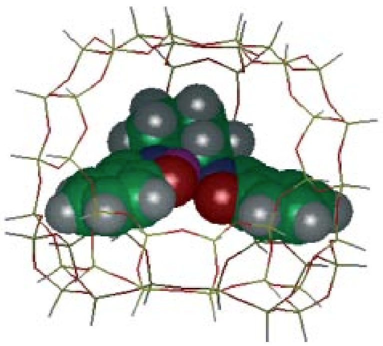
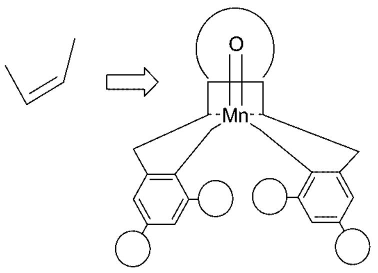


Figure 3. Molecular model of chiral Schiff-base Mn^{III}−bis(salicylidene)cyclohexanediamine lacking *tert*-butyl groups encapsulated within zeolite Y

The low enantiomeric excesses obtained using zeolite-encapsulated complexes can be rationalised considering that the asymmetric induction requires, as determined in solution, a precise “*side-on*” approach of the alkene to the oxomanganese epoxidation centre, the role of the bulky *tert*-butyl substituents being to impede the approach from other directions (Scheme 6). This process is completely disrupted when the complex is encapsulated in the zeolite, the geometry of the voids being the main factor dictating the possible approaches between the guest and the alkene. In addition, the presence of other Mn species in the solid, particularly as Mn^{II}, that can act as unselective epoxidation centres, has also been determined by EPR spectroscopy and electrochemistry.[122,123]



side-on approach of the alkene to the encumbered Mn=O bond

Scheme 6

A Co^{II}−Schiff-base complex derived from *N*,*N′*-bis(salicylidene)-1,2-diphenylethylenediamine has also been encapsulated within zeolite by the template method and studied as co-catalyst for the ruthenium-catalysed oxidation of benzylic alcohols.[124] The resulting zeolite-bound complex shows several distinctive facts with respect to the same complex in solution including: (i) higher reaction rates due to site isolation; (ii) no need for triphenylphosphane as axial ligand; and (iii) relative lack of influence of the solvent in which the reaction is carried out.[124]

3. Ship-in-a-Bottle Systems as Photocatalysts

Besides being catalysts for thermal reactions, zeolite-embedded guests prepared by ship-in-a-bottle synthesis have also been widely used as photocatalysts. In this latter case, the solid absorbs light and converts it into chemical energy by generating a highly reactive species. The photocatalytic generation of the $^{\cdot}OH$ radical from O_2, H_2O_2 or other sources is an emblematic example of conversion of light into chemical energy. Photocatalysis is obviously less developed than catalysis but is showing great promise for air and water purification.

In the following sections we will describe examples of ship-in-a-bottle-prepared systems whose use as a photocatalyst has been described.

a. Transition Metal Complexes

i) Tris(bipyridyl)ruthenium and Related Poly(pyridyl) Complexes

Tris(bipyridyl)ruthenium was one of the first large guests for which a ship-in-a-bottle synthesis was reported. The initial synthetic procedure by Lundsford et al.[125] was later improved by Dutta.[126] The method consists of the initial introduction of $[Ru(NH_3)_4]^{3+}$ followed by addition of an excess of 2,2′-bipyridine and prolonged heating at 220 °C. The excess of ligand is removed by continuous solid-liquid extraction. Calzaferri has shown that the purity of the encapsulated $[Ru(bpy)_3]^{2+}$ complex decreases upon increasing the loading of the complex due to diffusion problems.[127]

Other species present as impurities have an $[Ru(bpy)_n(NH_3)_{6-2n}]^{2+}$ ($n < 3$) stoichiometry. However, essentially pure samples of included $[Ru(bpy)_3]^{2+}$ can be obtained for loadings lower than one complex for every two supercages.[127]

Tris(bipyridyl)ruthenium is a complex that exhibits a high phosphorescence quantum yield. Since this phosphorescence is quenched by oxygen, a sensor based on this ruthenium complex has been developed.[128] $[Ru(bpy)_3]^{2+}$ has also been a favourite probe molecule for studies dealing with photoinduced electron transfer as well as in basic studies on long charge storage.[125,126,129,130] These studies rely on the easy emission detection in opaque powders.

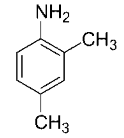
In an attempt to increase the efficiency of the charge separation, Dutta and co-workers reported the ship-in-a-bottle synthesis of tris(bipyridyl)ruthenium in nanometric zeolite X.[139] Caution has to be taken in this case to avoid acid formation during each step of the ship-in-a-bottle synthesis, since otherwise the crystallinity of the nanoscopic X zeolite is considerably reduced and the advantages of the use of nanocrystals disappear. Under conditions in which 90% of the crystallinity is preserved, it was observed that the photoinduced electron transfer between $[Ru(bpy)_3]^{2+}$ and methylviologen is about a factor of two more efficient in nanocrystals than in conventional micrometer-sized crystallites.[139]

Besides tris(bipyridyl)ruthenium(II) other metal−polypyridyl complexes such as $[Co(bpy)_3]^{2+}$,[140] $[V{=}O(bpy)_2]^{2+}$,[141] and $[Fe^{II}(bpy)_3]^{2+}$ [79,142] have also been synthesised. In the case of $[Fe^{II}(bpy)_3]^{2+}$, Bossmann, Braun and co-workers have studied the use of the resulting solid as a heterogeneous photo-Fenton catalyst.[142] In the Fenton reaction, aggressive $^{\cdot}OH$ radicals are formed by reaction of Fe^{II} with hydrogen peroxide [Equation (1)]. Then, this $^{\cdot}OH$ radical can initiate the oxidative degradation of the vast majority of organic molecules either by C−H hydrogen abstraction, nucleophilic addition to unsaturated multiple bonds or by single-electron oxidation. The Fenton reaction requires a stoichiometric amount of iron(II) with respect to the $^{\cdot}OH$ radical. A variant of this Fenton process that only requires catalytic amounts of Fe is the photo-Fenton reaction in which the Fe^{III} formed in Equation (1) is reduced back to Fe^{II} by light, with the additional generation of a second $^{\cdot}OH$ radical. One problem of this photochemical reaction is that the aquated iron ion has a low extinction coefficient in the visible region and therefore UV light is required. The advantage of the use of the $[Fe^{II}(bpy)_3]^{2+}$ complex is that it absorbs visible light with a high molar absorptivity, thus increasing the efficiency and practicality of Equation (2).

$$Fe^{2+} + H\text{-}OO\text{-}H \longrightarrow Fe(OH)^{2+} + {\bullet}OH \qquad (1)$$

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {\bullet}OH \qquad (2)$$

In a further refinement, these authors have co-doped the encapsulated $[Fe^{II}(bpy)_3]^{2+}$ with TiO_2 clusters that have been prepared after the ship-in-a-bottle synthesis of $[Fe^{II}(bpy)_3]^{2+}$ by hydrolysis of $TiCl_3$.[142] Apparently, the presence of TiO_2 enhances the photocatalytic activity of the iron complex by acting as an electron relay from the donor to the iron(III) complex. The photocalytic activity of this $[Fe^{II}(bpy)_3]^{2+}$ system in acidic aqueous solutions has been studied in the presence and absence of H_2O_2 using 2,4-xylidine, a recalcitrant non-biodegradable pollutant, as model compound.



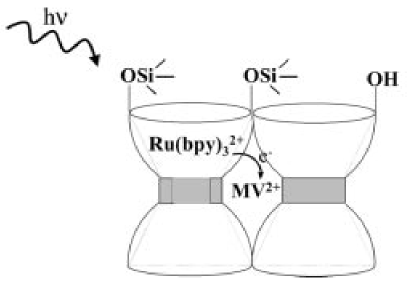
2,4-xylidine

Fundamental studies on electron transfer within the zeolite matrix have been done by using metal−polypyridyl complexes. For instance, Fukuzumi and co-workers have also synthesised $[Fe(bpy)_3]^{2+}$ encapsulated inside NaY at a loading of one molecule per 10 supercages and converted it into $[Fe(bpy)_3]^{3+}$ by chemical oxidation with chlorine.[143] Observation of an extremely slow reaction between ferrocene and encapsulated $[Fe(bpy)_3]^{3+}$ has led to the suggestion of the occurrence of a long-range electron transfer through the zeolite framework.[143] An analogous *through-framework* electron transfer between tris(bipyridyl)ruthenium and methylviologen has been demonstrated using ITQ-2 as zeolite (Scheme 7).[130] In this case, the zeolite defines a topology comprising external cups and internal 10-membered channels. The (polypyridyl)ruthenium complex is located in the open cups of the zeolite while viologen as electron acceptor is incorporated inside the 10-membered-ring channels of the zeolite. Upon photoexcitation of $[Ru(bpy)_3]^{2+}$, an electron transfer to encapsulated MV^{++} occurs.

b. Organic Cations

i) Pyrylium and Derivatives

The first ship-in-a-bottle syntheses in zeolites were used to prepare encapsulated metallic complexes. In most of these early cases, the key feature in the encapsulation was



Scheme 7

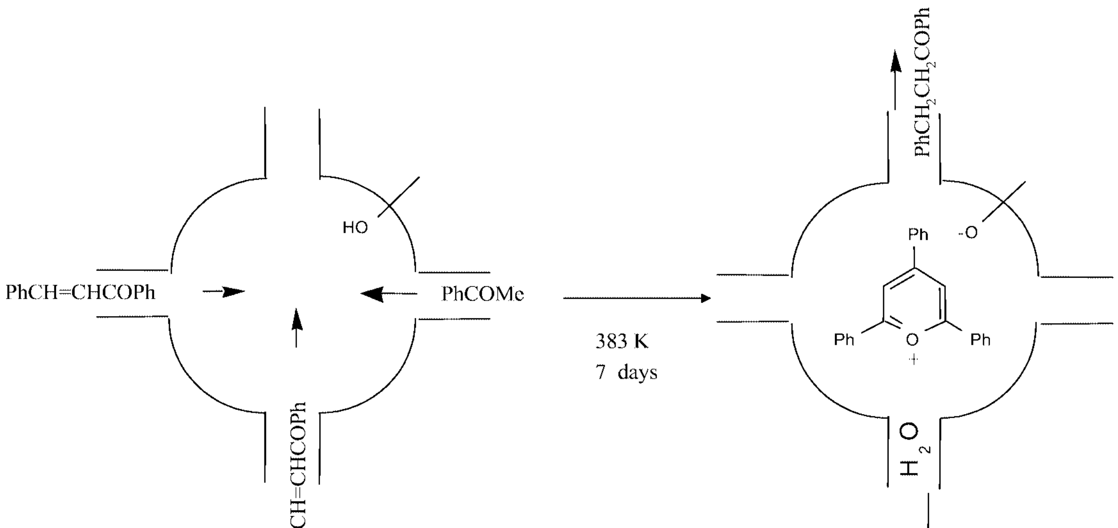
the formation of a coordinative bond between a metal ion and a heteroatom having lone electron pairs.

In contrast to this, the hallmark of organic synthesis is the formation of new C−C bonds by coupling of nucleophilic and electrophilic reagents in the absence of a metal. In this regard, one of the first ship-in-a-bottle *organic* (as opposed to coordination chemistry) synthesis was the encapsulation by Corma, Garcia and Miranda of the 2,4,6-triphenylpyrylium ion inside zeolite HY.[144] This pyrylium ion is obtained in solution by treating 2 equiv. of chalcone with acetophenone in the presence of strong liquid Brönsted acids, such as perchloric or tetrafluoroboric acid.[145] The reaction mechanism involves the aldol reaction of chalcone and acetophenone, followed by aromatisation by hydrogen transfer. By emulating this solution reaction successfully, but using the Brönsted acid sites of microporous HY zeolite instead of a liquid acid, it was possible to obtain the encapsulated 2,4,6-triphenylpyrylium (Scheme 8). Alternatively, the chalcone can be synthesised in situ catalysed by the same HY zeolite by allowing acetophenone and benzaldehyde to react.

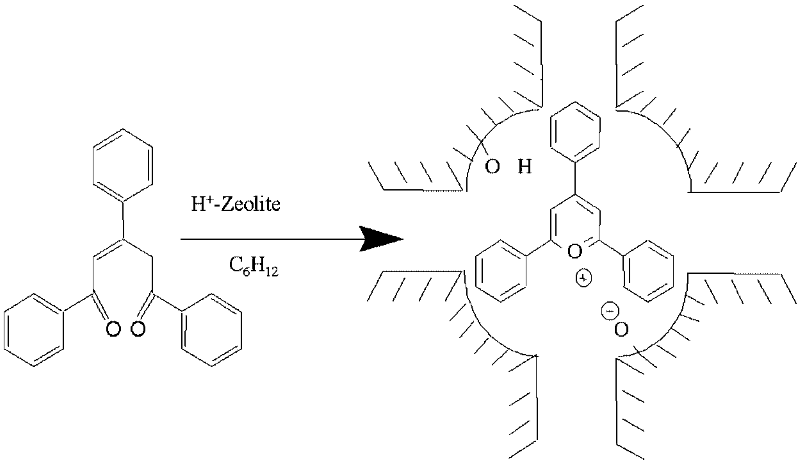
The above procedure requires HY samples of sufficient acidity to promote the aldolic condensation. Recently, Miranda, Braun and Bossmann have reported[146] a more simple procedure to perform the ship-in-a-bottle synthesis of 2,4,6-triphenylpyrylium. This recent process has the advantage of starting from the commercial HSO_4^- salt of 2,4,6-triphenylpyrylium and commercial NaY in aqueous suspension to achieve the encapsulation of the dye. Formally, the whole process is a true ion exchange in aqueous solution of a bulky, size-excluded 2,4,6-triphenylpyrylium ion by internal Na^+. All the available information indicates that under these conditions the pyrylium ion undergoes a hydrolytic ring opening and the more flexible 1,3,5-triphenyl-2-pentene-1,5-dione migrates inside the zeolite supercage (Scheme 9). Once inside, dehydration by mild baking of the solid reforms the pyrylium heterocycle. Among the many advantages of this improved procedure, the major ones are the purity reproducibility of the encapsulated 2,4,6-triphenylpyrylium, the use of neutral, commercial NaY and the possibility to control the loading of the pyrylium cation in a reproducible way to achieve essentially a complete filling of one dye molecule per supercage. Concerning reproducibility, the crucial step is the baking of the zeolite to accomplish the complete cyclisation of the pentenedione.

2,4,6-Triphenylpyrylium salts such as those with BF_4^-, HSO_4^- and ClO_4^- are soluble in organic solvents such as CH_2Cl_2, CH_3CN and alcohols. These salts of 2,4,6-triphenylpyrylium are well-known electron-transfer photosensitizers in organic solvents.[147] Analogously, 2,4,6-triphenylpyrylium@Y is a solid photocatalyst that is able to promote photoinduced electron-transfer processes in organic solvents, such as one-way (*Z*)/(*E*) isomerisation of stilbene[148,149] and Diels−Alder cyclodimerisation of 1,4-cyclohexadiene.[150] Moreover, 2,4,6-triphenylpyrylium@Y can also be an effective photocatalyst in aqueous solution while, as mentioned above, simple salts of TP^+ cannot be used in water at neutral or basic pH due to the hydrolytic ring opening. Thus, one interesting feature of the encapsulation is that the occluded 2,4,6-triphenylpyrylium becomes persistent in water and can be used as a solid photocatalyst in water.[151] When encapsulated inside zeolites, 2,4,6-triphenylpyrylium has been found to be an efficient photocatalyst for the degradation and partial mineralisation of pesticides in water upon solar light irradiation. Some of the pesticides that can be degraded by the photocatalytic irradiation of encapsulated 2,4,6-triphenylpyrylium are phenol, aniline, 4-chlorophenoxyacetic acid,[152] methylparathion,[153] fenvalerate[154] and propoxur.[155] The case of 2,4,6-triphenylpyrylium@Y constitutes an example of the opportunities of encapsulated guests in photocatalysis.

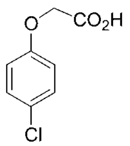
Evidence supports the proposition that the photocatalytic mechanism involves the generation of ˙OH radicals formed through photoinduced electron transfer from water



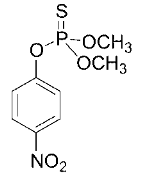
Scheme 8



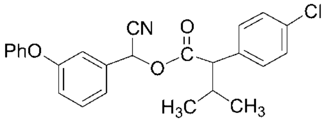
Scheme 9



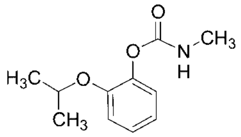
p-chlorophenoxyacetic acid



methylparathion



fenvalerate

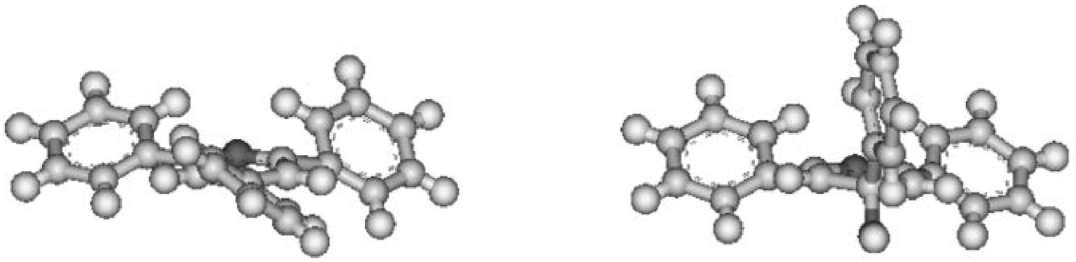


propoxur

to the dye in its excited state.[151] Interestingly, encapsulation also protects the dye from self-degradation by ˙OH. Even irradiation of a suspension of 2,4,6-triphenylpyrylium encapsulated within zeolites in distilled water produces the build-up of a 10^{-2} to 10^{-3} M concentration of H_2O_2.[151] This lack of self-degradation has been rationalised based on the molecular modelling that indicates that the zeolite framework binds the 2,4,6-triphenylpyrylium tightly and it does not allow the size increase required in the nucleophilic attack (Scheme 10).[151] Self-degradation is a common phenomenon that precludes the use of organic photosensitizers as photocatalysts. This conformational immobilisation of 2,4,6-triphenylpyrylium is also responsible for the observation of room-temperature phosphorescence.[156]

After the initial synthesis of 2,4,6-triphenylpyrylium and in an effort to improve its photocatalytic activity and stability, the ship-in-a-bottle synthesis of some derivatives was successfully accomplished. Thus, 2,4,6-triphenylthiapyrylium has been obtained encapsulated in zeolites Y and Beta by allowing acetophenone and benzaldehyde dissolved in cyclohexane to react in the presence of acid zeolites, wherein the solvent and zeolites have been previously saturated with H_2S (Scheme 11).[157] Compared to oxygen, the lower electronegativity of the S atom, similar to carbon, increases the aromaticity of the thiapyrylium ring and therefore its thermal stability. Also, the photocatalytic activity of 2,4,6-triphenylthiapyrylium is superior to that of the pyrylium analogue (Figure 4), 2,4,6-triphenylthiapyrylium encapsulated within zeolites Y and Beta exhibiting in addition a much higher photostability thus making possible its reuse.

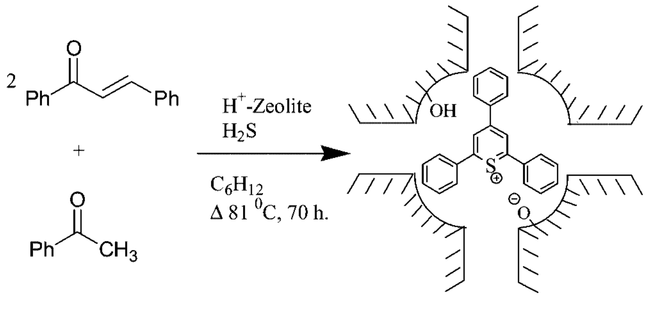
Tetraphenylbipyrylium is a bulky molecule that requires not one but two neighbouring supercages for it to be accommodated, thus making its ship-in-a-bottle synthesis especially challenging. The preparation of this dication inside the pores of zeolite Y has been accomplished employing the same reaction type as that followed for the synthesis of triphenylpyrylium, but using terephthaldehyde instead of



before attack

after nucleophilic attack; too large to fit into the zedite cavity

Scheme 10



Scheme 11

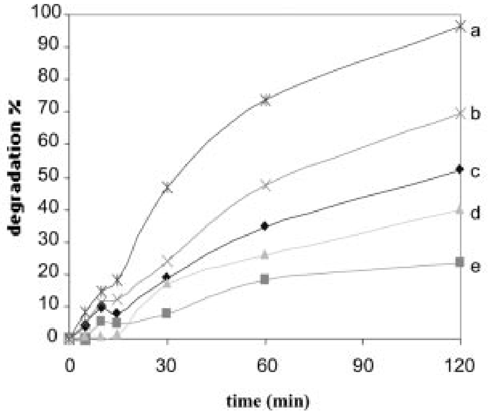


Figure 4. Plot of the phenol disappearance vs. time upon irradiation of an aqueous solution (20 mL) of phenol (δ = 40 ppm) in the presence of solid photocatalysts (30 mg) under identical conditions; a: 2,4,6-triphenylthiapyrylium@HBeta; b: 2,4,6-triphenylthiapyrylium@HY; c: P-25 TiO_2 standard; d: 2,4,6-triphenylpyrylium@HBeta; e: 2,4,6-triphenylpyrylium@HY

benzaldehyde.[158] Figure 5 provides a view of the model showing the tetraphenylbipyrylium occupying two zeolite Y supercages. However, although bipyrylium encapsulated within zeolite Y also exhibits the photocatalytic activity characteristic of 2,4,6-triphenylpyrylium, its efficiency is somewhat lower.

ii) Trityl Cations and Derivatives

Carbocations derived from the parent trityl cation are among the most stable in solution due to charge delocalisation through the aryl rings. Under appropriate conditions and in the absence of nucleophiles and moisture the parent trityl cation becomes indefinitely persistent in solution. Obviously, the presence of electron-donor substituents on the aryl rings stabilizes the carbocation further. One property of these trityl ions is the colour, which changes from the yellow of the unsubstituted trityl to orange, following the Woodward rules of additivity, according to the nature of the substituent. Some of these cations find application as dyes or pigments, malachite green and rose aniline being two examples among many others.[159]

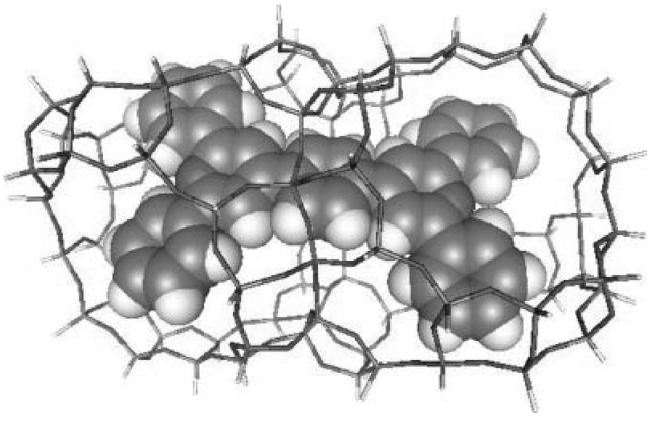
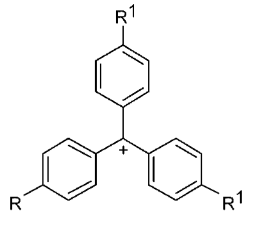


Figure 5. Model of tetraphenylbipyrylium showing the occupancy of two neighbour supercages (taken from ref.[158])



Trityl cations

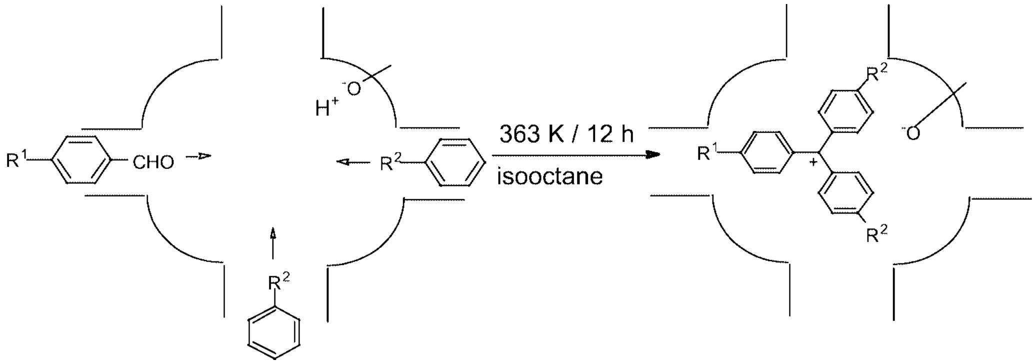
These trityl dyes have been prepared inside zeolite Y and Beta in their H^+ or La^{3+} forms by treating an aromatic aldehyde with electron-rich benzene derivatives such as anisole or *N*,*N*-dimethylaniline, as indicated in Scheme 12.[67,156] Evidence in support of the internal location of the dyes was obtained by the good fitting between the experimental high-resolution X-ray diffraction and the Rietveld refinement of a model in which the zeolite Y supercage contained the dye at one third of cage occupancy (Figure 6).[67] The resulting encapsulated dyes showed activity as heterogeneous photosensitizers to promote the radical-cation-mediated dimerisation of 1,3-cyclohexadiene.

Maciel and co-workers have followed a different strategy to form these encapsulated trityl cations consisting in the reaction of CCl_4 with benzene using the HY zeolite as catalyst. By using ^{13}C MAS NMR spectroscopy, isotopically labelled $^{13}CCl_4$ and studying the reaction of $Ph_3{}^{13}C^+$ with bulky nucleophiles, they reached the conclusion that the product was located predominantly in the internal cavities of the zeolites, in contrast to the simple adsorption of Ph_3CCl in HY that leads to the deposition of the bulky cation exclusively on the external surface of the particles.[160]

4. Ship-in-a-Bottle Systems as Electrocatalysts

Electrochemistry is a convenient tool to study the population of an electroactive guest located at the outermost supercages or subsurface zones since the electrochemical oxidation or reduction process has to be accompanied by the concomitant diffusion of a charge-balancing electrolyte. This diffusion limits the depth in which electrochemistry occurs in the particle.

One interesting application of zeolite-embedded guests is in electrocatalysis[161,162] and the development of selective electrodes.[163,164] In this case the electrode, normally a metallic conductor, is modified by depositing a film of a zeolite-



Scheme 12

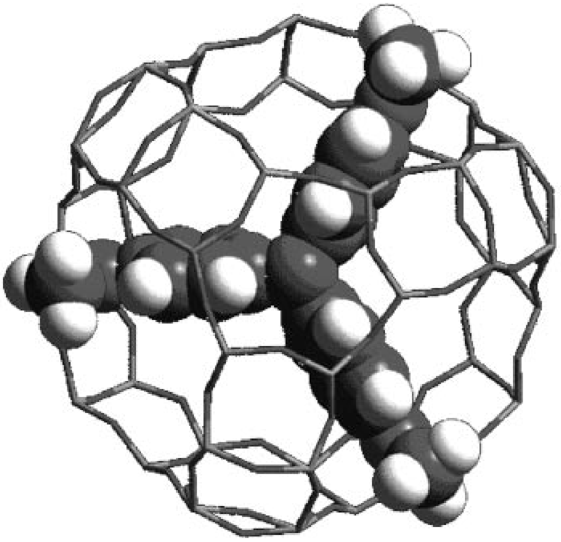


Figure 6. Molecular model of the tris(4-methoxyphenyl)methyl cation based on the Rietveld refinement of the high-resolution XRD pattern (taken from ref.[67]; reprinted with permission; © 1996 American Chemical Society)

encapsulated guest that increases the electrochemical response towards an analyte or promotes an electrochemical process.

Most of the transition metal complexes have a characteristic electrochemical response due to the changes in the metal oxidation number. By means of electrochemistry, Bedioui, Balkus and co-workers have provided experimental evidence of the site isolation arising from the encapsulation of a large guest in a single zeolite supercage. Thus, Rh^{III}−phthalocyanine@NaY exhibits a reversible reduction peak interpreted as the transition between Rh^{III}−phthalocyanine/Rh^{II}−phthalocyanine, while in solution this reversible reduction peak is not observed due to dimerisation/dismutation of the Rh^{II} species.[165]

Balkus, Jr. and Bedioui have prepared zeolite-encapsulated metal−salen compounds and studied their electrochemical response.[166] Apparently, the electrochemical behaviour of the encapsulated complexes is similar to that in solution and the redox potential peaks of the zeolite-encapsulated complexes appear at similar values as in homogeneous solution. In this context, an interesting controversy is how deep in the particle the electrochemical techniques can probe and if the electrochemical response is purely extrazeolitic, due to zeolite-bound complexes, or really intrazeolitic.[167−169]

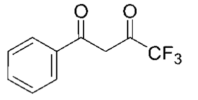
Organic guests can also exhibit an electrochemical response.[123,170−172] 2,4,6-Triphenylpyrilium encapsulated inside zeolites has been shown to promote the electrochemical response of dopamine, norepinephrine and other catecholamine neurotransmitters by a factor of up to 20. This can serve to develop electrodes that allow the detection of smaller concentrations of analytes that exhibit a selective response for a substrate.

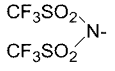
5. Ship-in-a-Bottle Systems as Sensors and Photochromic Systems

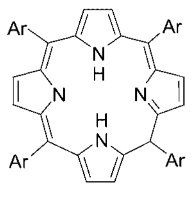
The large surface area, the porosity and even the shape-selective adsorption of zeolites are also very interesting for the development of solid sensors in which a zeolite-entrapped guest can report on the presence of certain analytes.

As mentioned earlier, metal−polypyridyl complexes such as $[Ru(bpy)_3]^{2+}$ are strongly photoluminescent either in solution or when encapsulated within zeolites. The actual emission decay kinetics is sensitive to the environment of the complex and to the presence of quencher molecules such as oxygen.

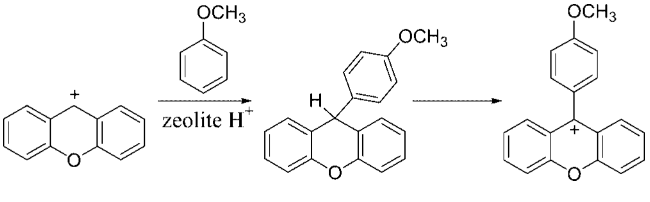
Rare-earth cations are also strongly luminescent, but in contrast to normal emission from organic lumophores, the atomic emission may consist of sharp atomic lines rather than broad emission bands. Luminescent rare-earth complexes have also been used as sensors.[173−176] However, atomic photoluminescence presents, in general, two problems. On one hand, the excitation of the atomic orbital of the cation is difficult since rare-earth cations do not absorb in the visible or even in the UV and light absorption is a prerequisite for the emission. On the other hand, the presence of water and other ligands containing O−H groups coordinating the rare-earth cation thwarts the emission by providing an efficient radiationless deactivation pathway consisting in the vibration of the O−H group in resonance with the decay of the excited atomic electronic state. Both problems can be overcome by complexation of the rare-earth cation. Formation of a suitable rare-earth complex prevents the quenching of water and at the same time it introduces new ligand-to-metal transition bands in the visible that allows easy excitation of the rare-earth cation. Encapsulation of these luminescent complexes within zeolites can serve to obtain a highly luminescent solid in which site isolation and compartmentalisation provided by the zeolite framework reduces the self-quenching and emission reabsorption that occurs in pure crystals of the complex. Photoluminescent Eu^{3+},[177] Nd^{3+} [178] and Tb^{3+} [179] complexes with trifluoroacetylacetophenone, bis(perfluoromethanesulfonyl)aminate or tetrarylporphyrinate have been prepared by ship-in-a-bottle synthesis within a series of zeolites.


4,4,4-trifluoro-1-phenylbutane-1,3-dione


bis(trifluoromethylsulfon)amidate


tetraarylporphyrin

9-(4-Methoxyphenyl)xanthylium has also been prepared by a ship-in-a-bottle synthesis inside the cavities of zeolites Y and Beta by electrophilic attack of preformed xanthylium cation[180] on electron-rich anisole (Scheme 13).[181] The resulting 9-arylxanthylium remains entrapped inside the zeolite supercages, molecular modelling indicating that the conformational rotation of the anisyl substituent over the xanthylium cores is impeded by the encapsulation (Figure 7). An interesting consequence of the conformational freezing in 9-(4-methoxyphenyl)xanthylium@HY is the observation of fluorescence. In solution these dyes do not emit at room temperature due to the efficient radiationless deactivation mechanism consisting in the flipping of the electron-rich anisyl group around the electron-poor xanthylium moiety, the observation of room-temperature emission for 9-(4-methoxyphenyl)xanthylium@HY is taken as an experimental confirmation of the molecular model of the 9-anisylxanthylium encapsulated within zeolite Y supercages. In a certain sense, encapsulation has the same effect as decreasing the temperature, both methodologies diminishing the conformational mobility. Photoluminescence from encapsulated 9-(4-anisyl)xanthylium is quenched by nucleophiles and this quenching can be the basis for the development of sensing systems.



Scheme 13

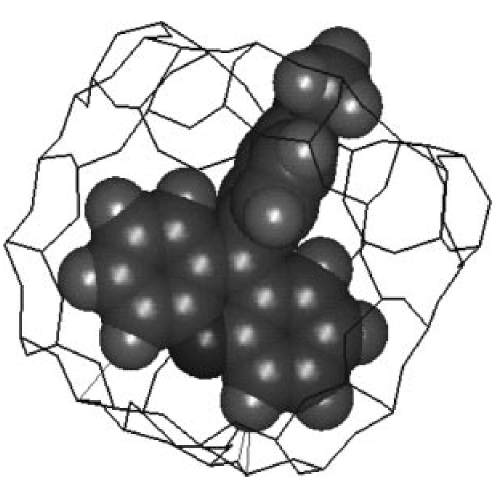
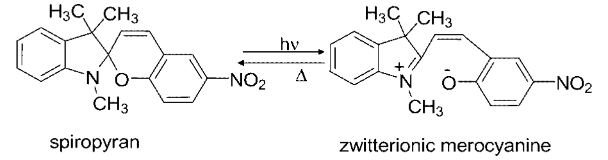


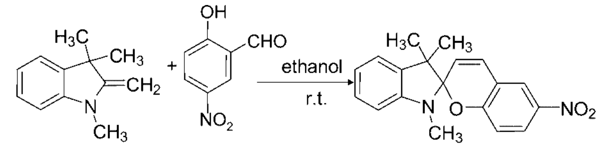
Figure 7. Molecular model of the 9-(4-methoxyphenyl)xanthylium cation encapsulated within an *all-silica* zeolite Y supercage (taken from ref.[181]; reprinted with permission; © 1996 American Chemical Society)

Spiropyrans with a chromene substructure are typical photochromic compounds in solution.[182] Upon illumination of the colourless spiro form, ring opening with formation of the merocyanine isomer leads to the development of colour, depending on the actual substitution of the spiropyran (Scheme 14). Upon standing in the dark, the thermodynamically unstable open merocyanine isomer undergoes thermal ring-closure back to the spiropyran form (Scheme 14).



Scheme 14

For some applications as photochromic pigments it would be of interest to support spiropyrans on a solid. The molecular size and the conformational rigidity of the spiro form precludes adsorption of these chromotropic compounds inside the cavities of faujasite, and a ship-in-a-bottle synthesis is required. This has been accomplished by Garcia et al. by treating 1,3,3-trimethylindoline with 4-nitrosalicylaldehyde in the presence of zeolite NaY (Scheme 15).[183] In contrast, spiropyran can be adsorbed on mesoporous MCM-41[184] without requiring any synthesis.



Scheme 15

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However, although in situ spectroscopic characterisation and product studies have demonstrated the formation of encapsulated spiropyran, it appears that the reversibility of the ring opening and closure is strongly modified by the polar environment of the zeolite supercage and/or the presence of weak acid sites as compared to ethanol solution. As a consequence, in a few irradiation/dark cycles the zeolite-containing spiropyran becomes strongly coloured and this colour does not disappear upon standing in the dark. These facts have been interpreted as indicating that in the zeolite the open merocyanine form tends to become stabilized, protonated and (*Z*)/(*E*)-isomerized, in contrast to the rapid and selective cyclisation observed in solution (Scheme 14).

Azo dyes such as methyl orange adsorbed in mesoporous Y zeolites have been prepared by coupling of *N*,*N*-dimethylaniline with diazonium cations.[185] Apparently, the dimensions of the transition states are too large to fit inside the supercages of regular dimensions and as result the azo dyes are not formed in the cages, but in the mesopores formed by defects in the crystal structure of the zeolite. Zeolite Y can be specially treated with citric acid and similar strongly complexing organic hydroxy acids to promote the formation of mesopores by damaging partially the crystal structure. The resulting azo dye incorporated inside the zeolite can act as a pigment and fluorescent solid.

6. Ship-in-a-Bottle Systems in Molecular Switches

As mentioned in the Introduction, one of the novel potential applications of zeolite-encapsulated guests is as functional materials in nanotechnology. One of the current strategies in nanotechnology is the "*bottom-up*" approach in which a molecule comprising several subunits is designed on purpose to produce a given effect upon external stimulus. These functional molecules are frequently termed as molecular devices since they perform certain actions at the molecular level that are characteristic of common mechanical devices. One type of such molecular devices are the so-called molecular machines in which one unit of the molecule is able to perform a cyclic movement emulating, at the simplest level, a machine.[53,186,187] While many of these molecular machines have been synthesised and the proof of principle at the molecular level has been sufficiently demonstrated, one general problem in this area is how to organize and assemble the individual molecular machines so that a coherent and co-operative response can be obtained from the assembly. In this regard, zeolites may provide a compartmentalized and organized space in which the molecular machines can be entrapped and held in place on the surface of a given support.

A preliminary step towards the direction of assembling molecular machines is their synthesis inside the zeolite micropores. One of the most common components in molecular machinery is the so-called "blue box", which is a bipyridinium macroring that acts as an electron-poor moiety forming charge-transfer complexes with electron-rich subunits in rotaxanes and catenanes.[188] Figure 8 shows a model of this blue-box encapsulated within zeolites.

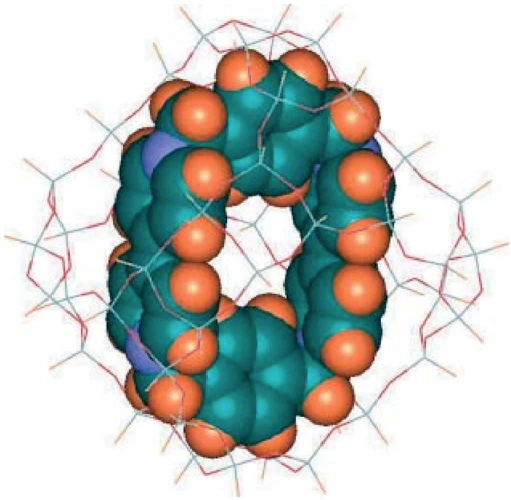


Figure 8. Molecular modelling of the bis(bipyridinium)cyclophane macrocycle inside the zeolite Y supercages

Besides spectroscopic characterisation, formation of the bipyridinium macrocycle was confirmed by dissolving the zeolite with HF and recovering the macrocycle from the solution.[188] The key factor in the success of the ship-in-a-bottle synthesis is the "*templating*" effect of the zeolite cavity approaching the distant pyridine N atoms in the open intermediate (Figure 9). The shape of the cage and the position of the positive charges in the same cage are responsible for the larger yield for cyclophane macrocycle formation inside zeolite Y than in solution, where the yield of cyclisation is only about 3%.

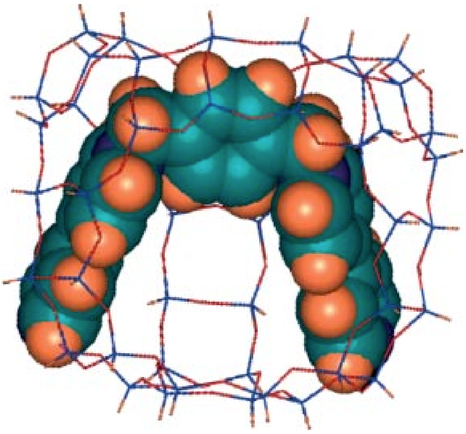
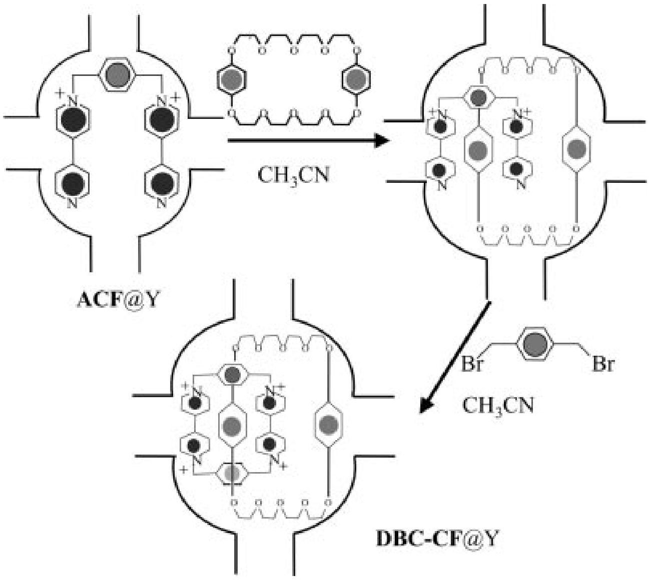


Figure 9. Molecular model of the open dicationic precursor of the blue box encapsulated within the supercage of zeolite Y; note the distance between the terminal N atoms (taken from ref.[188a]; reprinted with permission; © 2002 American Chemical Society)

A further development has been the ship-in-a-bottle synthesis of a [2]catenane comprising the *blue box* interlocked with a hydroquinolyl polyether macrocycle. The ship-in-a-bottle synthesis parallels the route followed in solution for this [2]catenane, initiating the procedure by ion-exchanging the precursor in the zeolite (Scheme 16).



Scheme 16

Upon photochemical excitation at the charge-transfer band of the [2]catenane an electron transfer and a corresponding charge separation occur (Figure 10). The most important effect of the encapsulation of the catenane inside the zeolite has been the observation of a dramatic enhancement of the lifetime of the viologen radical cation. In solution the geminate radical ion pair generated instantaneously upon excitation of the charge-transfer complex lives in the picosecond time regime and this short lifetime makes the operation of any co-conformational[189] and atomic movement that could occur in the state of charge separation generated as a consequence of the photoinduced electron transfer impossible. Co-conformational changes would occur in the microsecond or longer timescale. In this regard, the above results have demonstrated that encapsulation of these molecular switches inside the zeolite would increase the lifetime of the radical cation sufficiently to allow movements of the interlocked rings, but the actual occurrence of these co-conformational changes is yet to be demonstrated.

7. Ship-in-a-Bottle Synthesis of Conducting Polymers

Conducting organic polymers such as polyacetylenes, polyanilines and polypyrrols have promising applications in the field of charge storage, as antistatic coatings and in electronics. A general problem associated with conducting polymers is their degradability upon exposure of the charged polymer to the atmosphere. A way to circumvent this decomposition is to encapsulate the polymers within the pores of zeolites that will protect them from the attack of external reagents. The field of encapsulated polymers has been subjected to periodic reviews.[190−193] Among the most recent contributions are the preparation of parent polyacetylene by polymerisation of acetylene in Ni-exchanged zeolites, essentially filling the void volume.[194,195] Electrochemical measurements indicate that the polymer can be charged, but the polymer becomes degraded in the first use.[196] The spontaneous formation of polarons has also been reported.[197] Spange has recently reviewed the cationic polymerisation of vinyl ether, furan and other polymers within MCM-41.[198−200]

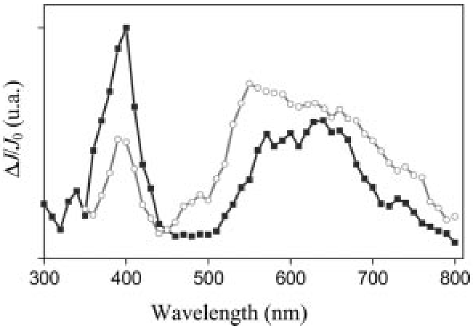


Figure 10. Diffuse reflectance UV/Vis transient spectra recorded for the catenane (circles) and for the bipyridinium cyclophane (squares) encapsulated within the supercages of zeolite Y (data taken from ref.[188b]; reproduced by permission of The Royal Society of Chemistry)

C. Concluding Remarks

Since the initial, seminal work of Herron and Schulz-Ekloff on the ship-in-a-bottle synthesis of metal complexes, a considerable number of examples of this and other types of guests have been reported. These reports have continued to explore the application of zeolites containing encapsulated guests as catalysts and zeozymes, but other fields like photocatalysis, electrocatalysis, sensors and development of functional materials have also benefited from ship-in-a-bottle methodologies. In the near future, and given the current impetus in nanotechnology, it can be anticipated that the systems based on the ship-in-a-bottle synthesis will attract renewed interest in order to develop active components for photonics (laser cavities, harmonic generators, light switches, wave guides, etc.) and as intelligent devices such as activable membranes, chromotropic layers. Also, the ship-in-a-bottle synthesis could find applications in molecular machines as a way to assemble and modify the properties of supramolecular systems.

The special properties of zeolites as hosts in terms of site isolation, space compartmentalisation, polarity and the presence of acidic and other sites are very interesting and can contribute to the operation and design of these hybrid solids. This field will also benefit from the continuous advances in the characterisation techniques, some of which have become routine, allowing a safer and firmer determination of the encapsulated material as well as from the preparation of zeolite films on substrates.[201,202]

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