DALTON
PERSPECTIVE

A unified approach to zeolites as acid catalysts and as supramolecular hosts exemplified

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Selected examples of different acid-catalysed reaction types are given to provide a unified approach to the activity of zeolites either to form products of interest which diffuse into the gas or liquid phase (heterogeneous catalysis) or to generate encapsulated organic material immobilised inside the zeolite cages with interesting photochemical, optical and electronic properties (material science). The central point of these highlights is to demonstrate that the knowledge gained in catalysis by zeolites can be applied to develop novel materials.

Heterogeneous catalysis *versus* materials science

Zeolites were first introduced as catalysts for large-scale gas-phase reactions in petrochemistry. Reactions such as cracking and aromatic isomerisation and disproportionation, showed the advantages of zeolites compared to conventional liquid acids in terms of easy separation of the reaction mixture, reactor design, control of the outcome of the reaction, shape selectivity effects, and the possibility to regenerate the catalyst after deactivation.[1] The results of the gas-phase reactions triggered an intense research aimed at developing the potentialities of zeolites for general acid-catalysed organic reactions in the liquid phase under batchwise conditions. During the last two decades an increasing number of publications have appeared reporting the use of zeolites as solid catalysts for organic reactions in the liquid phase for the production of fine chemicals. By now, heterogeneous catalysis of organic reactions by zeolites is a mature field. Since the seminal contribution of Venuto at the end of the 60s,[2] comprehensive reviews have periodically been published covering the reaction types reported in the presence of zeolites, the nature of the zeolite active sites and the effects that can be achieved.[3–6]

Zeolites are a large family of crystalline aluminosilicates wherein the framework defines channels and cavities of strictly regular dimensions on the nanometer scale.[7–9] These rigid internal voids termed as micropores are accessible to organic substrates provided that their molecular dimensions are smaller than the size of the pore apertures of the zeolite. Depending on the crystal structure of the zeolite, micropores of different dimensions and geometries are available (Scheme 1).

When using zeolites as heterogeneous catalysts, their activity progressively decays during the course of the reaction until eventually the solid becomes totally deactivated. In some cases, this decay has proved to be caused by leaching of active sites, particularly when the nature of the active sites contains heteroatoms that normally are not present in the framework composition of a regular zeolite. However, normally the major contribution to zeolite deactivation is the formation of undesired large molecules and even coke that leads to blockage of the micropores. From the point of view of the catalysis, these by-products or poisons are undesired materials and their nature and composition is not relevant unless they shed some light on the reaction mechanism.

In fact, studies aimed at determining the composition of the poisons formed during a given chemical reaction are very scarce. Even more, most of them deal with vapor-phase hydrocarbon cracking where the poisons have been determined to be formed by a complex mixture of polycyclic aromatic hydrocarbons as well as their partially hydrogenated derivatives.[10] From the limited number of cases studied, it is widely accepted that poisoning is generally due to the formation of intractable mixtures but this may turn out not to be true when performing other reactions with substrates containing functional groups under different experimental conditions of temperature and reaction media.

This general belief in heterogeneous catalysis contrasts with a large number of reports showing that it is possible to synthesise a fairly pure organic guest encapsulated within the zeolite micropores.[11] The simplest incorporation procedure consists in

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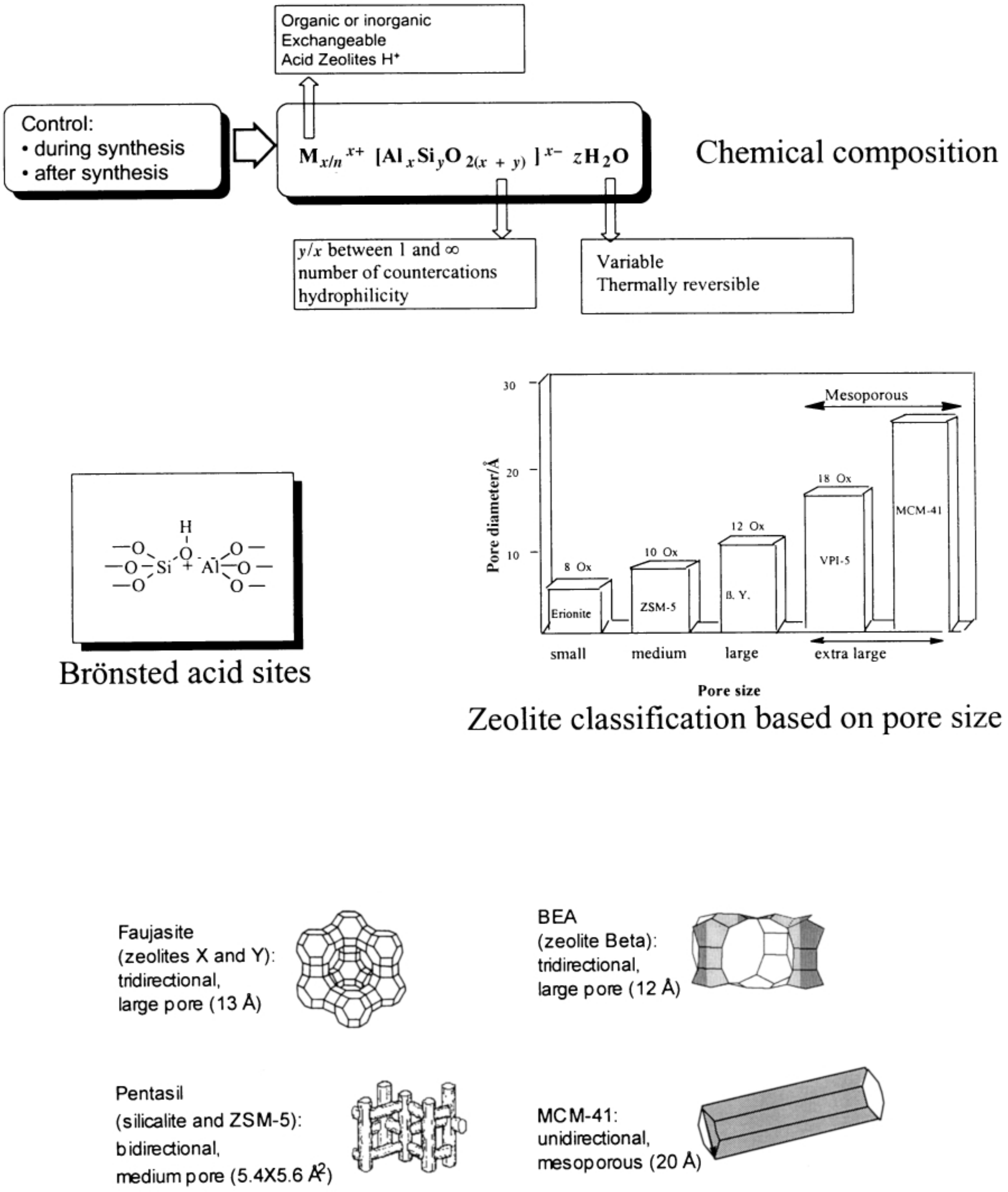


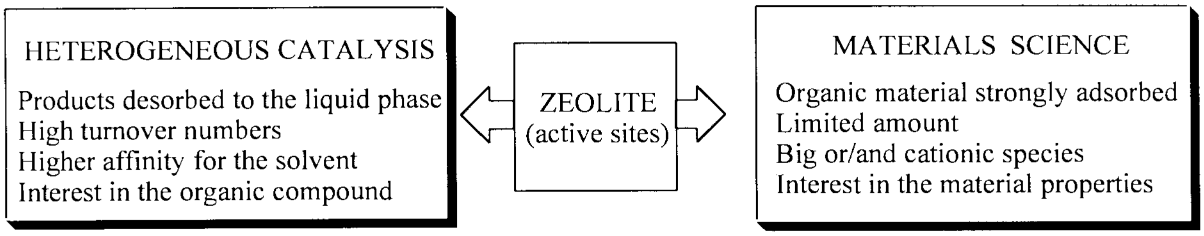
Scheme 1 Pore topology of some common zeolites and related MCM-41 aluminosilicate.

the adsorption from the liquid phase of a convenient precursor that at most undergoes simple functional group transformations. However, as the organic guest–zeolite systems move to higher levels of sophistication preparation of the encapsulated guests requires specific reactions that are able to be carried out highly selectively on the target organic species entrapped inside the pores. The most characteristic step in these cases is the creation of new carbon–carbon bonds that are the hallmark of organic syntheses. In many instances too, the reaction leading to the formation of the encapsulated species requires active sites and, in this regard, the zeolite is acting again as a catalyst. Below we will comment upon some syntheses in which these active sites are actually needed.

In the case of tridirectional zeolites having large cavities interconnected through smaller apertures, large molecules can be formed and accommodated inside the cavities, but they are unable to diffuse through the apertures. When these species are purposely formed, their preparation is often described as *ship-in-a-bottle* synthesis. When these bulky species are not the target of the process, their formation leads to the deactivation of the zeolite as a catalyst.

Therefore, the situation is that a microporous solid having catalytic sites forms products that are either (i) predominantly desorbed and diffuse into the reaction media, or (ii) they are retained inside the pores leading to new materials with interesting photochemical, optical, electronic or catalytic properties. While in catalysis a given site can form many product molecules, in the second case the maximum amount of encapsulated material is obviously limited by the pore volume of the zeolite and, typically the turnover number of a site is practically unity.

The products present in the liquid phase and those adsorbed inside the pores derive from common reaction pathways, but they can be totally different molecules. This justifies why some of them preferentially desorb towards the liquid phase while others are strongly retained within the internal voids of the zeolite. We have found two common features in most of the



Scheme 2 The catalytic activity of the zeolites can be used for two different purposes.

encapsulated organic material that rationalise the preference for the micropores: either (i) the molecular size is large enough to impede their diffusion, or/and (ii) they are positively charged species.

Given that the crystal lattice of the zeolite is negatively charged, the electroneutrality principle requires the presence of the corresponding number of positively charged species. These cations have to be accommodated within the internal voids in close proximity to the negative Al. The high polarity of the internal voids together with geometrical restraints to nucleophilic attacks favour the generation and stabilisation of organic cations within zeolites compared to other homogeneous media.

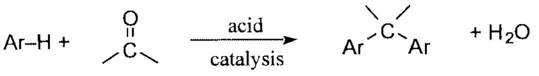
One particular case that is very important from a catalytic point of view is when the charge-balancing cation is formally a proton. Then, the zeolite behaves as a solid acid.[6] In this case, generation of a persistent carbocationic poison would lead to the substitution of the proton, leading to the immediate deactivation of the zeolite by neutralisation of the Brönsted acid sites. In addition, these carbocationic poisons can display other undesired effects such as the blockage of the pores, restricting intracrystalline diffusion.

In the present highlights we will present a unified approach to the catalytic activity of zeolites from two different perspectives. Thus, the same reaction type used in heterogeneous catalysis giving rise to high conversions of the substrates and leading to products can serve to produce highly selectively other species encapsulated within the zeolite pores. The species adsorbed can be totally different, albeit related, to the products observed in the liquid phase. While from the heterogeneous catalysis point of view this phenomenon can be described as poisoning, it can serve to prepare useful hybrid materials with applications in materials science (Scheme 2). The compartmentalised space defined by the zeolite crystal structure provides an ordered medium in which to assemble at the molecular level a system comprising different interconnected components.

Although related work aimed at the characterisation of the organic species formed inside the zeolite micropores and exploitation of their properties has been done by other research groups, given the space limitation of the present account herein we will focus mainly on different cases studied in our group.

Friedel–Crafts hydroxyalkylation of arenes *versus* triarylmethyl cation encapsulation

A reaction type that we have extensively studied over the years is the Friedel–Crafts hydroxyalkylation of arenes with aldehydes and ketones (Scheme 3).[12–15] This reaction is known to be acid-catalysed and is typically carried out using $AlCl_3$.[16] The use of Brönsted acids has been reported mainly for the intramolecular versions such as the Pechmann and the Bischler–Napieralsky synthesis. These intramolecular cyclisations are the only practical examples of hydroxyalkylations that are of synthetic interest.



Scheme 3 Hydroxyalkylation of arenes with carbonylic compounds.

In fact, in spite of the availability of the starting materials, this reaction has found only a limited synthetic application due to its lack of selectivity and the complexity of the reaction mixtures that are commonly obtained using conventional catalysis. Oligo- and poly-meric tars together with a variety of condensed polycyclic aromatic compounds are normally formed accompanying the expected diarylalkanes. In cases where the starting materials are highly reactive such as phenol and formaldehyde, the reaction cannot be controlled and high molecular weight polymers are formed (bakelites or novolacs).

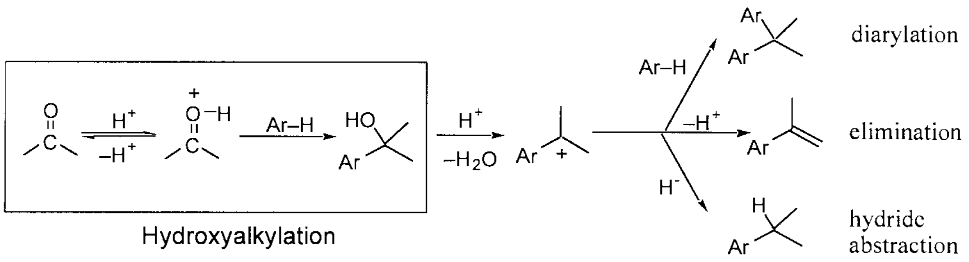
The accepted reaction mechanism is shown in Scheme 4, wherein the key reaction intermediates are the benzylic alcohols. Although the name of the reaction derives from these intermediates, they are too reactive and upon protonation and dehydration either a second arylation or formation of a C=C double bond occurs.

Formaldehyde, in its solid polymeric form, reacts with an excess of benzene in the presence of acid zeolites to afford diphenylmethane in high conversion and excellent selectivity. From the influence of the level of Na^+-to-H^+ ion exchange it was established that this reaction is catalysed by the population of strong acid sites, *i.e.*, those with pK_a 0. This was concluded because while the total number of acid sites increases linearly as the Na^+-to-H^+ exchange progresses, titration of the acid strength distribution reveals that the population of strong sites increases exponentially with the Na^+-to-H^+ exchange.[17] Thus, an exponential relationship between the initial diphenylmethane formation rate and the percentage of Na^+-to-H^+ exchange reveals that not all the acid sites introduced by ion exchange are active to catalyse this reaction, but only that fraction whose population increases exponentially (Fig. 1).

Importantly, the Si/Al ratio of the zeolite chemical composition plays a significant role on the activity of the catalyst. Thus, by performing the benzene–formaldehyde reaction using a series of Y zeolites differing in the Si/Al ratio it was established that those zeolites having higher Si/Al ratios are more active compared to those with low Si/Al ratios (Fig. 2). Although we will deal later with this point in deeper detail, the effect of the Si/Al ratio is related to the deactivation of the catalyst. Those zeolites having a higher density of acid sites (low Si/Al ratio, high Al content) undergo faster deactivation by blockage of the pores with bulky species than those others where the sites are further apart which exhibit a slower activity decay and more prolonged service life.

Likewise, hydroxyalkylation of arenes and heteroarenes using aliphatic aldehydes can also be catalysed by acid zeolites, although the selectivity is reduced by the possibility of diarylation or C=C double bond formation leading to 1,1-diarylalkanes and 1-arylalk-1-enes, respectively.[18] These two product types are also formed in the hydroxyalkylation with aliphatic ketones.[18]

A case of particular importance here is the hydroxyalkylation of benzaldehyde and its derivatives with electron-rich aromatic compounds (Scheme 5). In this case, together with the expected triarylmethanes the reaction mixture contains a variable amount of diarylmethanes, where a scrambling of substituents from the benzaldehyde and the arene has occurred.[14,19]



Scheme 4 Mechanism of hydroxyalkylation and common consecutive processes.

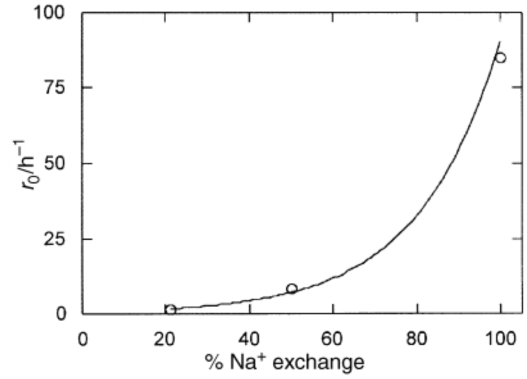


Fig. 1 Exponential relationship between the initial reaction rate of diphenylmethane formation (r_o) at 80 °C and the percentage of Na^+-to-H^+ exchange of the NaHY catalyst.

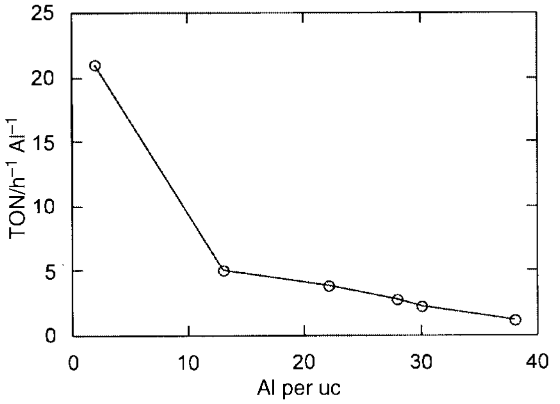
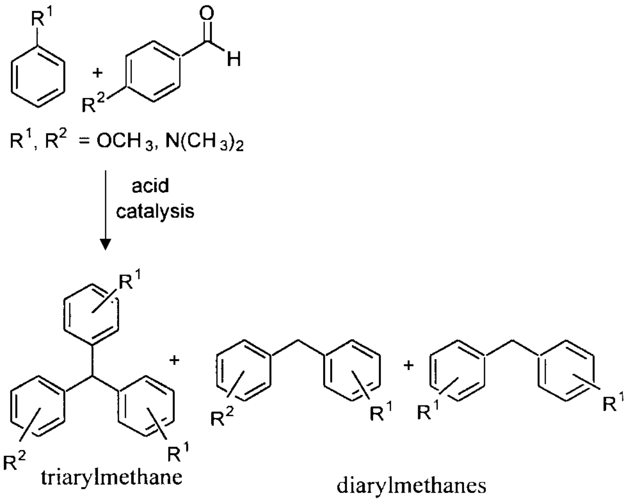


Fig. 2 Turnover number (TON, defined as: initial rate/Al per uc) for the zeolite Y-catalysed alkylation of benzene (50 ml) with formaldehyde (200 mg) at 80 °C *versus* the number of Al per unit cell (uc) of the catalyst.



Scheme 5 Common products of the reaction of benzaldehyde with electron-rich benzene derivatives.

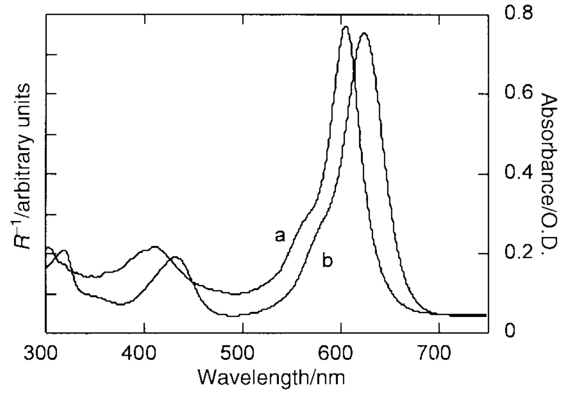


Fig. 3 Diffuse-reflectance (R^{-1}) and transmission (O.D.) UV-vis spectra of malachite green incorporated inside zeolite Y (curve a) and in CH_2Cl_2 solution (≈10^{-4} M) (curve b), respectively.

Importantly, depending on these substituents, the catalyst develops a characteristic colour (from orange, red to green) concomitantly with the progress of the reaction.[19]

It turns out that analytical and spectroscopic characterisation of the deactivated catalyst after the reaction reveals the presence of fairly pure triarylmethyl cations. These cations have characteristic UV-vis spectra that have been frequently used to detect spectroscopically these intermediates in the presence of their colourless precursors.[20] As an example, Fig. 3 shows a comparison of the diffuse-reflectance UV-vis spectrum of the HY zeolite after its use as a catalyst for the hydroxyalkylation of *N*,*N*-dimethylaniline with benzaldehyde with a commercial sample of the chloride of bis(*N*,*N*-dimethylaniline)phenylmethyl cation (*malachite green*) in CH_2Cl_2.

Likewise, IR spectroscopy confirms unambiguously the formation of these triarylmethyl cations (trityl cations) by comparison of the IR spectra of zeolite wafers with those of authentic samples of trityl cations when possible (Fig. 4). For the tris(4-methoxyphenyl)methylium–HY hybrid the high-resolution X-ray diffractrogram (HR-XRD) showed diffuse electron density inside the zeolite Y supercages and the Rietveld refinement of the HR-XRD could be fitted to an organic cation–zeolite hybrid structure (Fig. 5) that is coincident with the visualisation obtained by molecular modelling.

Encapsulation of trityl cations inside the cavities of tridirectional Y and β zeolites leads to a remarkable degree of control of the molecular properties of the incorporated guests.[21] This results in some interesting properties of the hybrid material. Thus, trityl cations do not emit in solution due to an efficient radiationless deactivation mechanism consisting in the swinging of the aryl rings around the empty p orbital of the central trivalent cationic carbon. In order to be operative, this non-emissive decay requires conformational mobility. Perusal of the model shown in Fig. 5 reveals that these cations are rigidly held by the zeolite matrix and the substituents in the *para* position are partially penetrating through the windows connecting neighbouring cavities. This tight fit of the zeolite matrix holding the trityl guest largely thwarts the conformational mobility, *freezing* the carbocation in its best docking inside the cavity. As a result of this, the trityl–zeolite hybrid materials exhibit

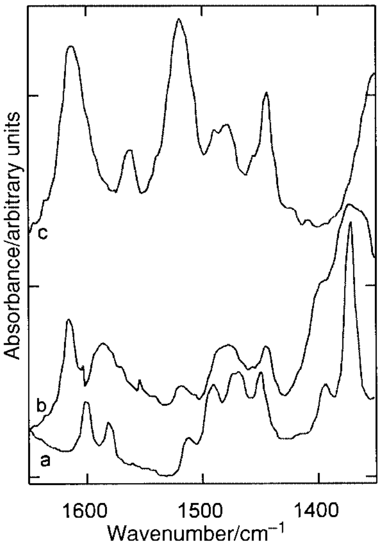


Fig. 4 Aromatic region of the FT-IR spectrum of malachite green incorporated inside Y zeolite after degassing for 1 h at 100 °C (curve a). The spectra (b) and (c) correspond to the malachite green chloride (coincident with the species within the zeolite) and to the different leuco form, respectively.

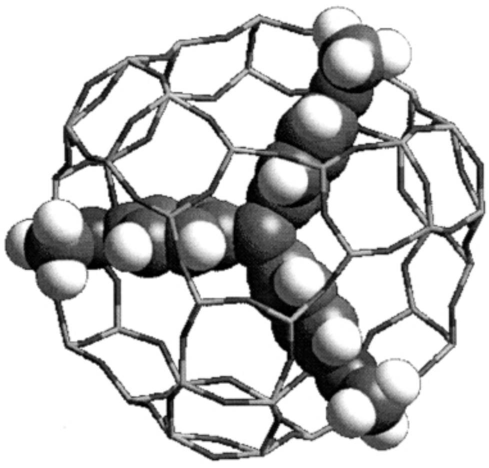
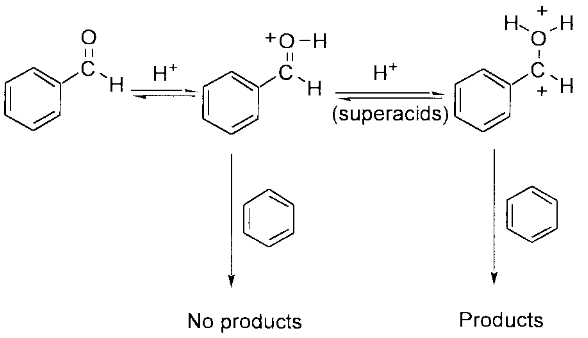


Fig. 5 Visualisation of the best Rietveld fit to the experimental HR-XRD of tris(4-methoxyphenyl)methyl cation inside the zeolite Y supercage.

fluorescence, the corresponding emitting singlet excited state decaying on the nanosecond time scale.[22] Furthermore, we have used these materials as heterogeneous photosensitizers for the dimerisation of cyclohexa-1,3-diene.[19,21]

One question that is crucial for the purpose of this account is how to connect the *abnormal* formation of diarylmethanes, observed as products in the liquid phase, and the formation of trityl cations inside the pores. To compound the puzzle, it is worth commenting upon the failure to obtain the unsubstituted trityl cation encapsulated inside zeolite Y. This species would result in the hydroxyalkylation of benzene by benzaldehyde, a reaction that in the presence of HY at 80 °C only takes place in very low conversions (<5%). This reaction has recently attracted much attention because it has been shown that it requires superacids as catalysts in order to occur at low temperature.[23,24] It has been shown that the electrophilic species attacking the benzene ring at low temperature is the doubly O,O-diprotonated benzaldehyde (Scheme 6).

Different methods of titration of the acid strength distribution of the H$^+$-form of zeolites have concluded that they lack superacid sites.[25,26] This is likely to be the reason why benzaldehyde does not react with benzene in the presence of HY zeolites at moderate temperatures. In order to promote this reaction using acid zeolites much higher temperatures are required.



Scheme 6 Superacid hydroxyalkylation of benzene with benzaldehyde at low temperature.

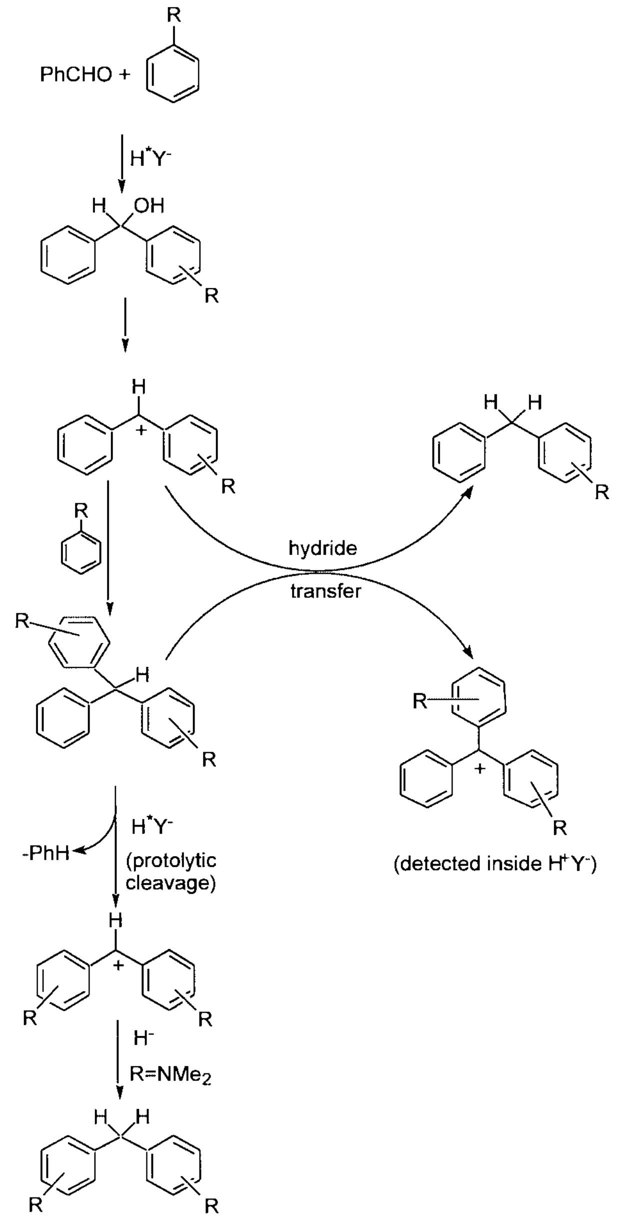
Thus, working in an autoclave at 150 °C, a 40% conversion of benzaldehyde with an excellent selectivity to triphenylmethane is achieved.[27] Diphenylmethane was not formed in significant amounts. Interestingly, spectroscopic characterisation of the catalyst as well as product analysis after disaggregation of the zeolite with HF revealed that besides that found in the liquid solution a significant amount of triphenylmethane was also entrapped inside the zeolite supercages. The molecular size of triphenylmethane is so big that after its formation in the internal voids it cannot diffuse through the windows and remains immobilised inside the cages.

In view of these results it is reasonable to assume that in the other cases where trityl cations are formed the immediate precursor should also be the corresponding triarylmethane. Loss of hydride will render the final observed carbocations. The question is, then, what species are acting as hydride acceptors and why they do not generate the unsubstituted trityl cation.

A reasonable answer has been obtained through a careful determination of the mass balance of the reaction.[27] Thus, the total moles of diarylmethanes formed coincides within the experimental error with the amount of encapsulated trityl cation. For those arenes where the product distribution is dominated by diarylmethanes, the catalyst is heavily loaded with the corresponding trityl cation. This supports the hypothesis that the hydride acceptor species generating the trityl cations are the diarylmethyl cations formed as reaction intermediates, the thermodynamic stability of the final carbocation being the driving force of the process (Scheme 7). The hydride transfer process requires long lived diarylmethyl cations since this pathway competes with the electrophilic attack on the solvent. Time-resolved measurements have revealed that given its relative instability compared to the other diarylmethyl cations of the series, the lifetime of the diphenylmethyl cation generated by laser flash within acid zeolites is on the microsecond time scale.[28] This lifetime is much too short to lead to any opportunity for intervention in hydride transfer processes.

As a confirmation of the above unified mechanistic interpretation for the product distribution outside and inside the zeolite pores, an experiment was carried out in which a sample of zeolite Y containing triphenylmethane (from the condensation of benzaldehyde and benzene) was treated with 4,4′-dimethyldiphenylcarbinol. This diarylcarbinol is a precursor of the 4,4′-ditolylmethyl cation which in turn should live long enough to abstract a hydride from triphenylmethane, thus, generating encapsulated trityl cation within the zeolite and ditolylmethane in the organic solvent. As a matter of fact, the parent trityl cation could be spectroscopically characterised in this way (Fig. 6) while simultaneously ditolylmethane was observed in the solution.

We will come back later to the importance of hydride transfer processes as a general way to generate carbocations as *poisons* within the zeolite pores. A more comprehensive review on the way that carbocations can be generated within zeolites has been published elsewhere.[29]



Scheme 7 Generation of trityl cations through hydride transfer from triarylmethanes to diarylmethyl cations.

Hydroxyalkylation of heterocycles with aldehydes *versus* encapsulation of macrocycles

A variant of the Friedel–Crafts hydroxyalkylation is the condensation of five-membered ring heterocycles such as furans and pyrroles by aldehydes and ketones. In contrast with the reaction of benzaldehyde with benzene, these electron-rich heterocycles are so reactive that the alkylation can be conveniently catalysed at room temperature by weakly acidic zeolites. Even more, the use of strong acids not only does not have any extra bonus in the process, but on the contrary, significantly reduces the selectivity of the catalyst by favouring polymerisation, opening of the heterocycle and the formation of intractable reaction mixtures.

In fact this reaction nicely exemplifies a crucial point in catalysis, *i.e.*, it is not the reaction type that has a common catalyst general for all the substrates, but each particular set of reagents depending on their higher or lower reactivity has a specific optimum strength requirement of the acid sites. The result of this is that different catalysts are needed for the same reaction type with different substrates. In this regard, zeolites are superior heterogeneous catalysts because, by varying the chemical composition and the conditioning treatment, their acid strength distribution can be fine tuned within a wide range to suit the demand of a given transformation.

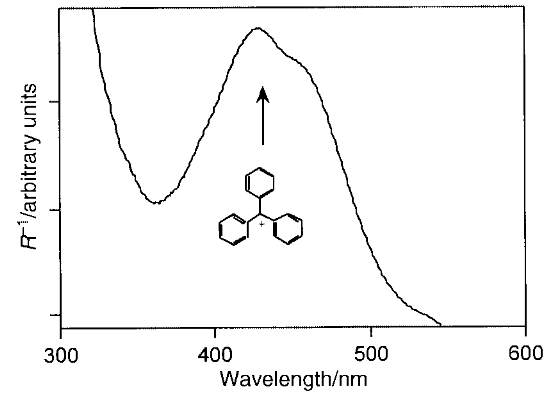
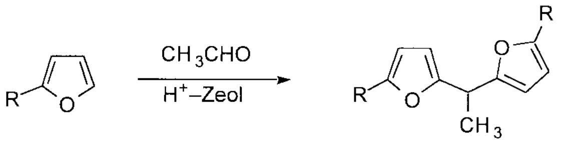


Fig. 6 Diffuse-reflectance UV-vis spectrum of a HY zeolite containing triphenylmethane after refluxing it with 4-methyldiphenylcarbinol. The visible bands between 400 and 500 nm are characteristic of the triphenylmethyl cation.

Thus, 2-alkyl furans react at mild temperature with aldehydes and ketones in the presence of the H^+-form of medium- and large-pore sized zeolites to afford *gem*-difurylalkanes in high conversions and selectivities (Scheme 8).[18]

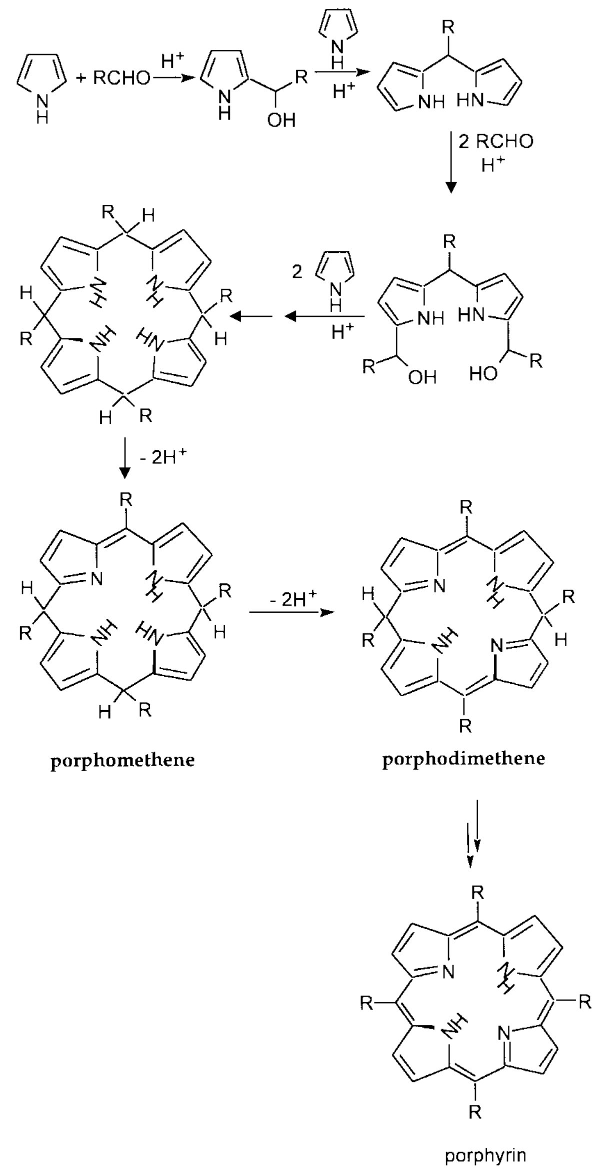


Scheme 8 Major product of the hydroxyalkylation of 2-alkylfuran with acetaldehyde.

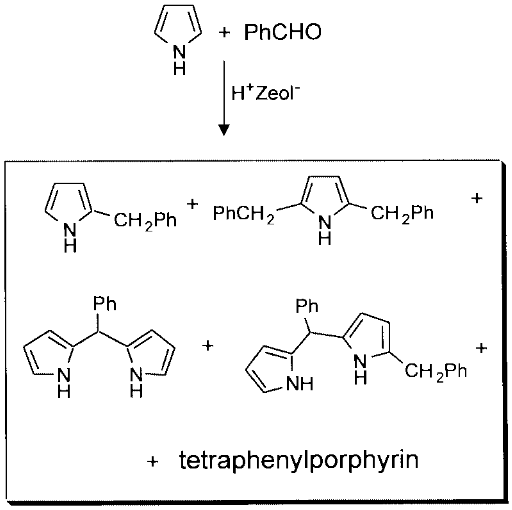
Monosubstitution at the α position of the heterocycle is necessary to avoid the formation of oligo- and poly-mers, as well as macrocyclic tetramers. In fact, *meso*-substituted porphyrins can be synthesised by direct condensation of aldehydes and pyrroles, followed by a spontaneous air oxidation (Scheme 9). Although the yield of this direct process is pretty low (8–15%), the simplicity of this one-pot procedure compared to alternate multi-step strategies makes the former an advantageous synthetic option.[30] Like in the case of furan alkylation, this tetramerisation is catalysed by weak acids such as acetic acid or transition metal ions acting as Lewis acids. In the latter case, a metal porphyrin complex, rather than the free ligand is the final species obtained.

The hydroxyalkylation of pyrrole with aldehydes in the presence of zeolites affords a second example of a process in which the product distribution in the liquid phase is different from the species that is present within the pores of tridirectional large-pore zeolites at the end of the process, the reason being the larger steric demand of the final products compared to their immediate precursors. Thus, periodic controls of the liquid phase during the course of the reaction of pyrrole and benzaldehyde in the presence of HY allow the detection of the corresponding *meso*-tetrasubstituted porphyrin, accompanied by variable amounts of mono- and di-pyrrole alkylation intermediates (Scheme 10).[31] The presence and concentration of porphyrin can be conveniently followed by UV-vis spectroscopy of the reaction mixture given that these macrocycles have a characteristic UV-vis spectra completely specific to these 18 π-electron aromatic macrocycles and totally different from the other reaction products. Thus porphyrins exhibit a Q band in the UV and a series of *Soret* bands in the visible region of much lower extinction coefficient (Fig. 7).[30]

A priori, a likely possibility would be that a fraction of these macrocycles would also be formed inside the zeolite cavities and, therefore, immobilised within the pores. However, the diffuse-reflectance UV-vis spectra of the catalysts after the



Scheme 9 Mechanism of formation of porphyrin by condensation of pyrrole with aldehydes showing the protoporphyrin precursors (porphomethene and porphodimethene).



Scheme 10 Products observed in the liquid phase for the reaction of benzaldehyde and pyrrole.

reaction in which porphyrins are present in the liquid phase clearly shows that these aromatic macrocycles are not present inside the zeolite (Fig. 8).

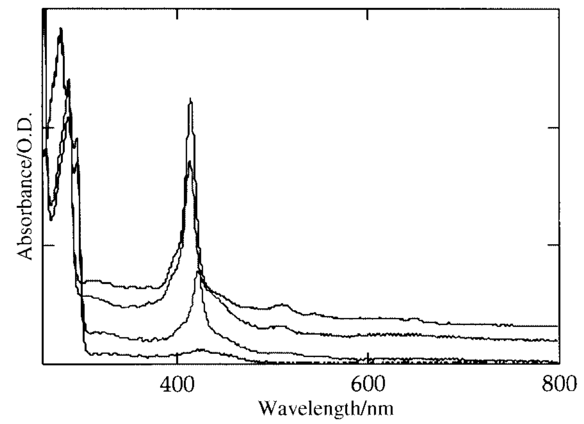


Fig. 7 UV-vis spectra of the organic phase taken periodically during the condensation of pyrrole and benzaldehyde in the presence of HY as catalyst.

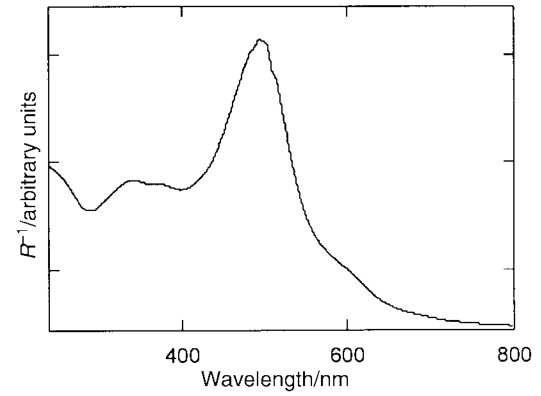


Fig. 8 Diffuse-reflectance UV-vis spectrum of the HY catalyst after the condensation of pyrrole and benzaldehyde. Figs. 7 and 8 correspond to the same reaction.

In fact, the UV-vis spectrum shown in Fig. 8 closely resembles that of protoporphyrins, the pyrrolic macrocyclic precursors of porphyrins prior to oxidation. Given the stability of porphyrins, this oxidation step is fairly easy and normally takes place spontaneously in the presence of atmospheric oxygen. Alternatively, mild oxidants such as quinones can be used.

To firmly support the theory that the organic material entrapped within the zeolite were protoporphyrins, a thoroughly extracted catalyst exhibiting the spectrum of Fig. 8 was disaggregated with hydrofluoric acid. Upon dissolving the zeolite matrix, the colourless supernatant becomes coloured in a few minutes exhibiting the characteristic porphyrin UV-vis spectrum.[31] This indicates that although the material inside the zeolite is not yet porphyrin it is easily transformed into it.

Molecular modelling provides a reasonable explanation to understand why protoporphyrins rather than porphyrins are formed inside the pores (Fig. 9).[31] Thus, the oxidation step introduces a remarkable decrease in the conformational freedom of the protoporphyrins, transforming them into rigid, flat porphyrins. The macrocycle coplanarity is a prerequisite introduced by the aromaticity of the macrocyclic ring, but it produces a significant increase in the molecular size of the guest. We suggest that this increase in the molecular dimensions of the guest is the factor thwarting in the zeolite the otherwise favourable oxidation process. The restricted volume of the reaction cavity in which the species is accommodated impedes the formation of porphyrin which only takes place after the massive destruction of the zeolite lattice with HF. Clearly, the zeolite lattice discriminates between protoporphyrins that are less bulky and more flexible and porphyrins that are larger and more rigid molecules.

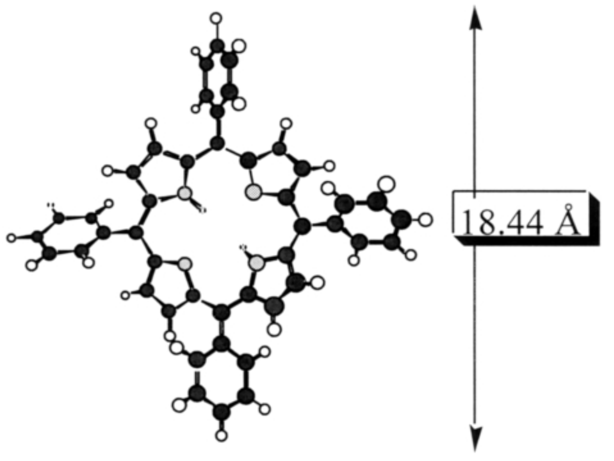
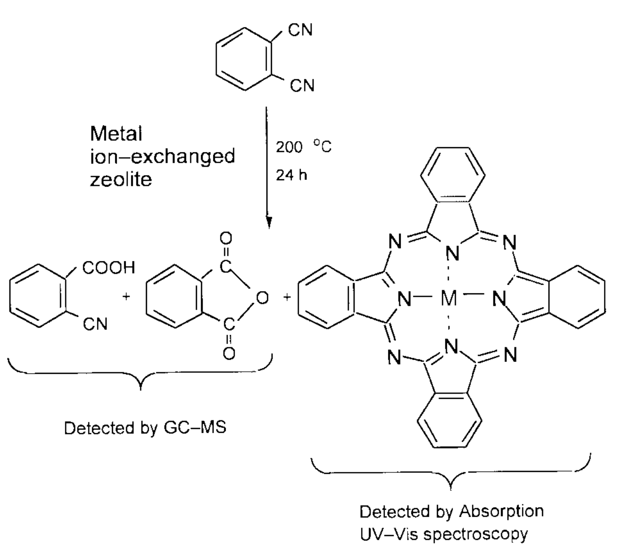


Fig. 9 Molecular mechanics modelling of tetraphenylporphyrin.

A similar case related to porphyrins is the ship-in-a-bottle synthesis of phthalocyanines within transition metal ion exchanged Y zeolite and mesoporous MCM-41 aluminosilicate, by tetramerisation of phthalonitrile (Scheme 11). The resulting encapsulated transition metal–phthalocyanine complexes have in turn found application as hydrocarbon oxidation catalysts, exhibiting a higher activity and turnover number than the unsupported, highly-insoluble complexes.[32–35] Given their large molecular size (≈14–15 Å), phthalocyanines are suggested to adopt a roof-like, bent conformation when encapsulated within the supercages of Y zeolite (13 Å diameter).[35,36] The extraordinary thermodynamic stability of phthalocyanines is the driving force toward their formation in spite of the fact that there is not enough room to accommodate the guest in the most favourable planar conformation.



Scheme 11 Products observed in the organic extracts after the reaction of phthalonitrile adsorbed in transition metal ion exchanged Y zeolites.

Friedel–Crafts aromatic alkylation with cinnamyl alcohols *versus* generation of phenyl-capped allyl carbocations

In the context of determining how chemo- and regio-selective the zeolites can be as acid catalysts, one paradigmatic example is Friedel–Crafts aromatic alkylation using allylic alcohols. These alkylating reagents encompass hydroxy and C=C double bond groups, both functionalities being able to intervene in Friedel–Crafts reactions depending on the catalyst and the reaction conditions (Scheme 12). In addition, the intermediate allylic carbocation has a delocalised positive charge and, depending on the transition state, the alkylation can take place regioselectively at the position of the hydroxy group or at this position plus the β-carbon with formal migration of the C=C double bond. We have studied in detail the alkylation of benzene derivatives and heterocycles with cinnamyl alcohol in the presence of acid zeolites.[37–39] In the case of cinnamyl alcohol, besides intermolecular processes common to allyl alcohols an intramolecular cyclisation leading to indene is also equally possible.

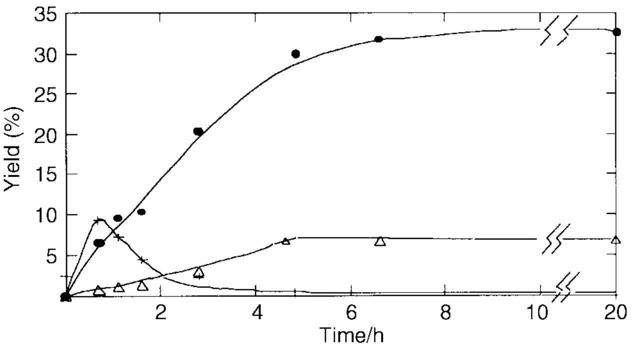


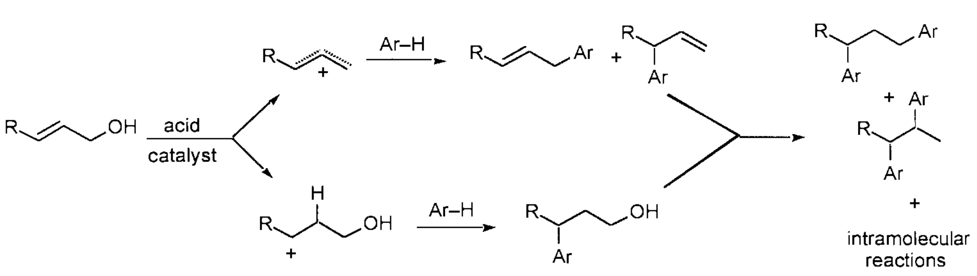
Fig. 10 Time–conversion curves for the reaction of cinnamyl alcohol with benzene at 80 °C in the presence of a HY catalyst: 1,3-diphenylpropene (+), 1-phenylindane (●), 1,1,3-triphenylpropane (△).

What we have generally observed is that using acid zeolites as catalysts the primary products are those arising from the chemoselective reaction of the hydroxy group.[38,39] For cinnamyl alcohol, this process is catalysed by sites of weak, medium and strong acid strength. Although dicinnamyl ethers are initially formed at low temperatures, they also can act as alkylating agents in the Friedel–Crafts process as the reaction progresses, especially at moderate temperatures. In contrast, Friedel–Crafts alkylation through the C=C double bond is only catalysed by strong acid sites (Scheme 13). Therefore, the final product distribution is highly dependent on the overall acid strength of the catalyst. As we have already mentioned, acidity in zeolites can be controlled to a large extent by simple ion-exchange or dealumination procedures. Among other advantages, this tunability is an important feature that make zeolites very appropriate as selective solid catalysts in organic reactions. Fig. 10 contains representative time–conversion plots showing the different evolution of the product distribution depending on the acid strength distribution of the zeolite.

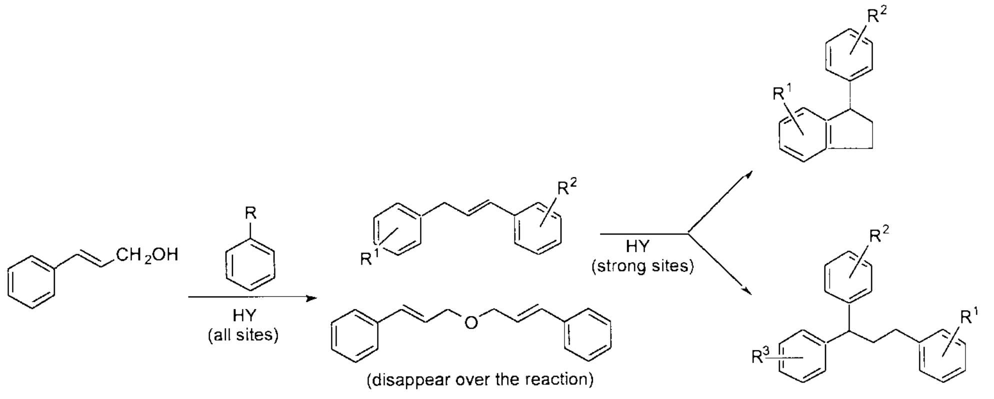
It is well-established that Al/MCM-41 exhibits only moderate acidity, notably lower than what can be achieved with microporous zeolites,[40] therefore, in spite of the potential advantages of mesoporous aluminosilicates in terms of the size of substrates and products that can access the internal surface, they have found only a limited application as acid catalysts.[41] These mesoporous aluminosilicates are appropriate catalysts only for those reactions requiring weak acid sites. This is the case for the reaction of bulky 2,4-di-*tert*-butylphenol with cinnamyl alcohol (Scheme 14), for which Al/MCM-41 was found for the first time to be more active and selective towards aromatic alkylation than modified Y zeolites or amorphous silica–aluminas.[37]

What is puzzling in the reactions of cinnamyl alcohol is that besides the expected products arising from the formal attack of the cinnamyl cation on the benzene derivative, the reaction mixture also contains variable amounts of isomeric 1,5-diphenylpentadienes.[38] These rather unexpected products derive exclusively from cinnamyl alcohol. Thus, blank reactions of cinnamyl alcohol in CCl_4 afford the same products (Scheme 15). Notably, the zeolite used as catalyst develops an intense, characteristic purple color during the course of the reaction, suggesting the presence of poisons with a conjugated, unsaturated chain.

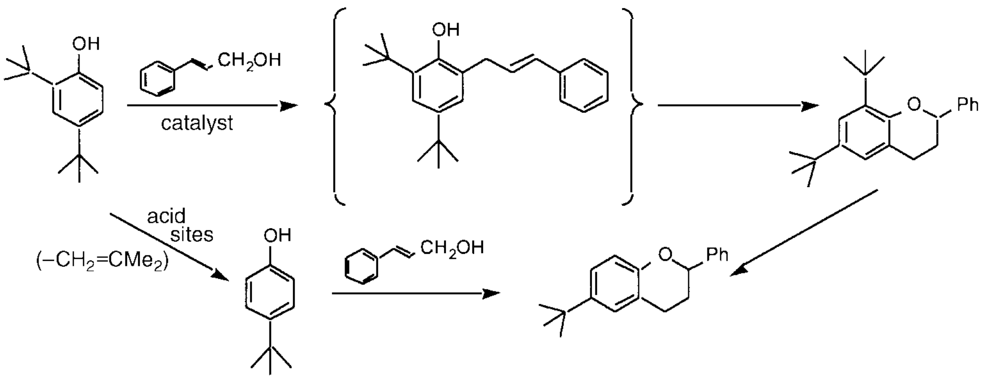
The structure of the organic species adsorbed within the catalyst could be unambiguously established as the 1,5-



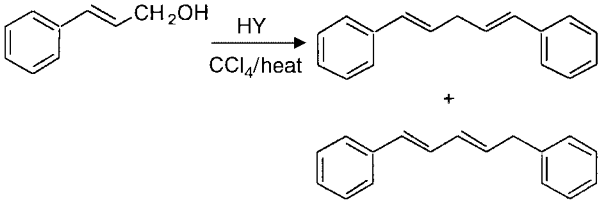
Scheme 12 Chemo- and regio-selectivity of allylic alcohols toward aromatic alkylation.



Scheme 13 Alkylation products observed in the reaction of cinnamyl alcohol in aromatic solvents using acid zeolites as catalysts.



Scheme 14 Products observed in the alkylation of bulky 2,4-di-*tert*-butylphenol with cinnamyl alcohol. Owing to the large molecular size and the low acid strength requirements, Al/MCM-41 was found to perform better as a catalyst than was Y zeolite.



Scheme 15 Unexpected dimerisation products of the self reaction of cinnamyl alcohol in the presence of acid zeolites.

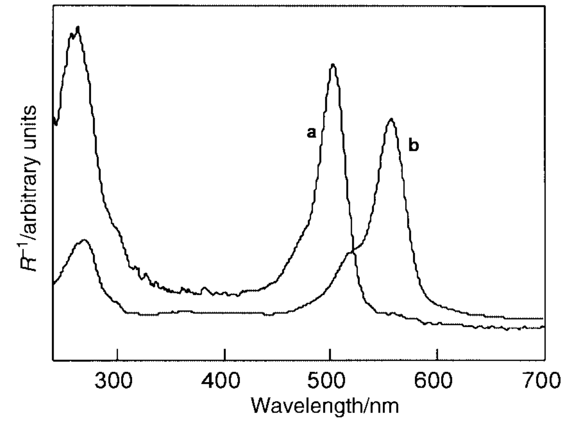
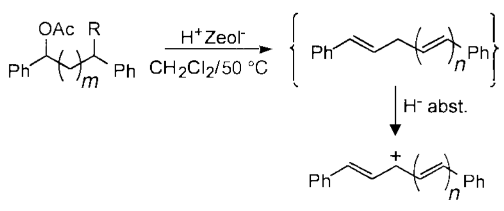


Fig. 11 Diffuse-reflectance UV-vis spectra of 1,3-diphenylpropenylium (curve a) and 1,5-diphenylpentadienylium (curve b) within ZSM-5 obtained upon adsorption of acetoxy derivatives of α,ω-diphenylalkanes.

diphenylpentadienyl cation by comparison of the diffuse reflectance UV-vis with those reported for this diallylic cation.[42] Furthermore, adsorption of an immediate precursor of this delocalised pentadienyl cation such as 1,5-dichloro- or 1,5-diacetoxy-1,5-diphenylpentane or even 1,5-diphenylpentadiene also gives rise to the same UV-vis spectrum characteristic of the 1,5-diphenylpentadienyl cation (Fig. 11). In addition, the 1,3-diphenylpropenyl cation can be generated in a similar manner (Fig. 11) by adsorption into acid zeolites of 1,3-dichloro- or 1,3-diacetoxy-1,3-diphenylpropane or 1,3-diphenylpropene (Scheme 16).

Generation as persistent species of the parent unsubstituted allyl cation is characteristic of superacid media,[26] and consequently previous attempts to characterise the allyl cation within the pores of ZSM-5 met with failure.[43,44] Working with superacids in liquid SO$_2$ solution, Olah and coworkers had established that the presence of phenyl rings do not introduce much thermodynamic stability to the allylic system.[45] This is due to the limited charge delocalisation through the aromatic nuclei. Therefore, in view of these precedents one should have prognosticated that the α,ω-diphenyl capped allylic carbo-



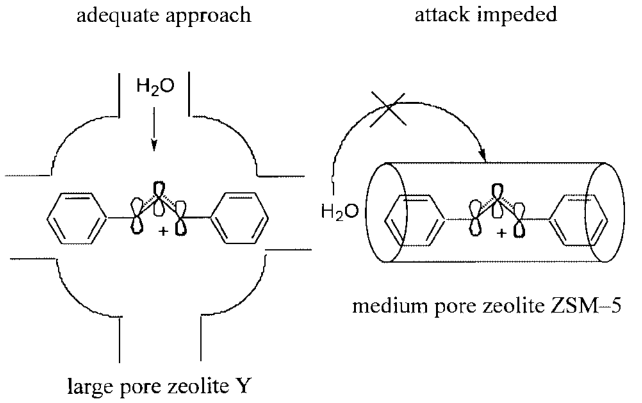
a: m=1, n=0, R=H; b: m=3, n=1, R=OAc
(only one of the resonance structures is shown)

Scheme 16 Generation of α,ω-diphenyl allylic cations by incorporation of acetoxy precursors within acid zeolites.

cations must not be formed within zeolites or, if formed, they would decay fast enough to not be detectable by conventional steady-state spectroscopy.

In sharp contrast to these predictions, some of these samples of propenyl and pentadienyl cations within the channels of ZSM-5 or even mordenite stored under ambient conditions are persistent for years. Furthermore, the zeolites containing these allylic cations can even be suspended in water and the colour remains for hours in the case of propenyl or indefinately in the case of pentadienyl. Notably, traces of water are known to quench these cations in solution.

To reconcile this dramatic persistence of α,ω-diphenyl capped allyl cations intubated within the zeolite channels with Olah's work in solution showing that the phenyl rings do not introduce much intrinsic thermodynamic stability on the allylic system, we have proposed that these substituents having a tight fit within the channels of some zeolites act like stoppers, protecting the inner allyl moiety from the attack of water (Scheme 17).[29]



Scheme 17 Pictorial representation of the stabilisation that the crystalline zeolite framework can exert on a reactive carbocation by impeding the attack of nucleophiles on the central allylic moiety of α,ω-diphenyl capped derivatives.

Clearly, water would still attack the positive allyl carbons, but the zeolite framework impedes water from reaching them.

The possibility of generating these allylic carbocations in an essentially neutral, rigid matrix (formally the H^+ sites are replaced by the allyl cation, and the zeolite becomes "deactivated" by neutralisation) has allowed us to control the molecular properties of these important organic reaction intermediates. Thus, none of these allyl cations show room temperature emission in solution due to conformational relaxation of the excited states. In contrast we have observed room temperature emission when they are incorporated within the zeolite voids.[46]

Interestingly, it has been predicted that the rotational energy barrier through the partial C–C double bonds of the allylic system should be high enough to allow the existence of stable *Z*/*E* stereoisomers (Scheme 18), although it has not been possible to detect them in solution probably due to a fast acid-catalysed *Z*/*E* isomerisation. The first time it has been possible to observe such stereoisomers as totally persistent species at room temperature has been after the photochemical *Z*/*E* isomerisation of the α,ω-diphenyl intubated within zeolites (Fig. 12).[46] One important factor contributing to the stability of these stereoisomers is that the photochemical reaction is performed in the absence of residual acidity.

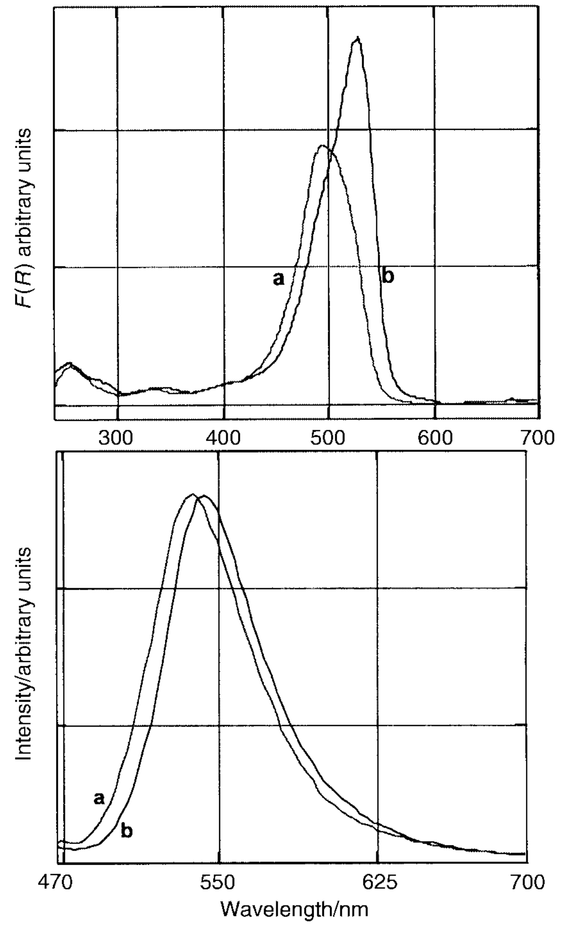
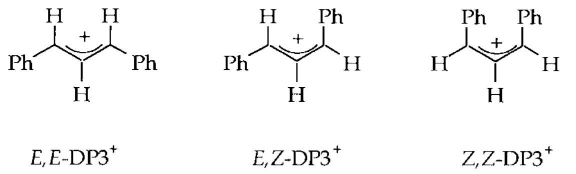


Fig. 12 Diffuse-reflectance UV-vis (top, plotted as the Kubelka–Munk function of the reflectance *R*) and emission (bottom, λ_{exc} = 500 nm) spectra of a sample of 1,3-diphenylpropenyl cation within H-ZSM-5 before (curve a) and after (curve b) irradiation. The shifts observed are interpreted as due to a *Z*/*E* isomerisation process.



Scheme 18 The three possible stereoisomers of 1,3-diphenylpropenyl cation ($DP3^+$).

Thus, acid zeolites can act as catalysts for the Friedel–Crafts alkylation with cinnamyl alcohol and deactivation occurs with formation of stable α,ω-diphenyl allyl cations. On the other hand, this reaction offers the possibility to generate and study diphenyl capped allylic cations in a neutral, rigid medium.

Dimerisation of styrenes and the controversial nature of the coloured organic species adsorbed within zeolites

Dimerisation of styrene can occur through several reaction mechanisms, including acid- or base-catalysed, radical, radical-ion and Ziegler–Natta catalysis. The product distribution can be taken as a fingerprint of the operating reaction mechanism and the type of intermediate involved in the process (Scheme 19 and Fig. 13).[47] We have shown that all the acid sites regardless

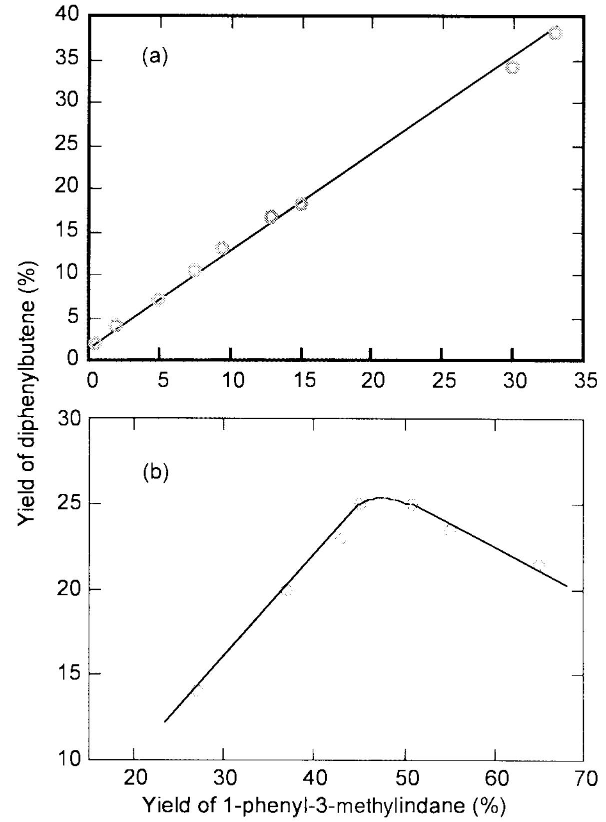
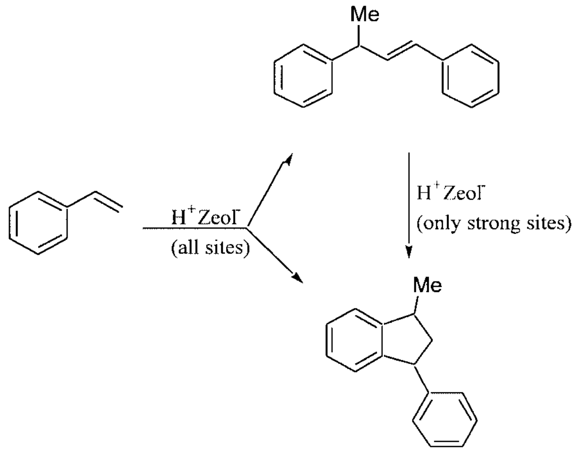


Fig. 13 Yield of the linear 1,3-diphenylbut-1-ene dimer *versus* the cyclic 1-phenyl-3-methylindane dimers in the reaction of styrene in the presence of HY-21 (a, weak acid sites) and HY-100 (b, stronger acid sites).



Scheme 19 Products of the acid-catalysed dimerisation of styrene. The cyclisation of the open to the cyclic dimer requires strong acid sites (see Fig. 13).

of their strength are able to catalyse the dimerisation of the parent styrene, but the subsequent cyclisation of the primary dimers occurs exclusively at the stronger acid sites.

If electron-donor substituents are present in the styrene moiety, the dimerisation is even faster. Therefore, it is not surprising that zeolites in their "supposedly" neutral Na$^+$-form can catalyse this reaction if some adventitious acid sites are developed during calcination or dehydration of the zeolite. This is the case for α-methylstyrene,[48] 4-methoxystyrene[49,50] and anethol[49] that, depending on the zeolite batch and its origin, can be adsorbed within the zeolite either as a monomer without any transformation or can react to form the dimers in an acid-catalysed mechanism. When dimerisation occurs, the zeolite becomes intensely coloured for all the styrenes, reflecting the formation of other species different from the final colourless dimeric products observed in solution. Considering the neutral products formed in the reaction and the similarity of the UV-vis spectra of the zeolites after incorporation of styrenes (Fig. 14) with that of the α,ω-diphenyl allyl cations (Figs. 11 and 12), the species were assigned to 1,3-diaryl allylic cations (structures shown on the top of Fig. 14). To support this assignment, the IR and ^{13}C NMR spectra of the species derived from 4-methoxystyrene were also recorded and the experimental spectroscopic data compared to those calculated by *ab initio* methods for 1,3-bis(4-methoxyphenyl)but-2-en-1-yl cation.[51] Since the spectra of this allylic cation was not yet reported, the good match between the experimental and the calculated spectra was taken as firm evidence for the correct assignment (Fig. 15).

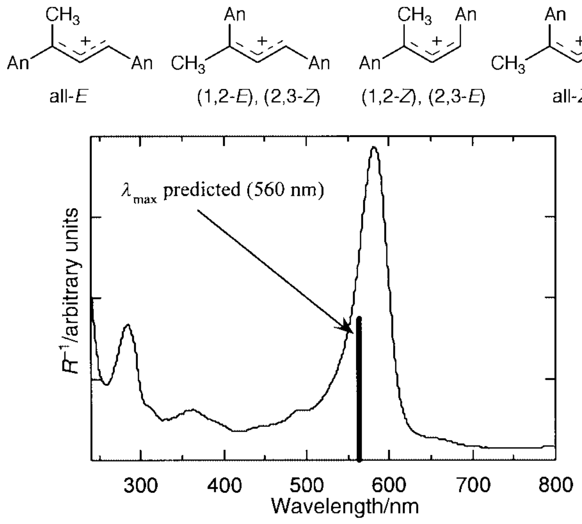
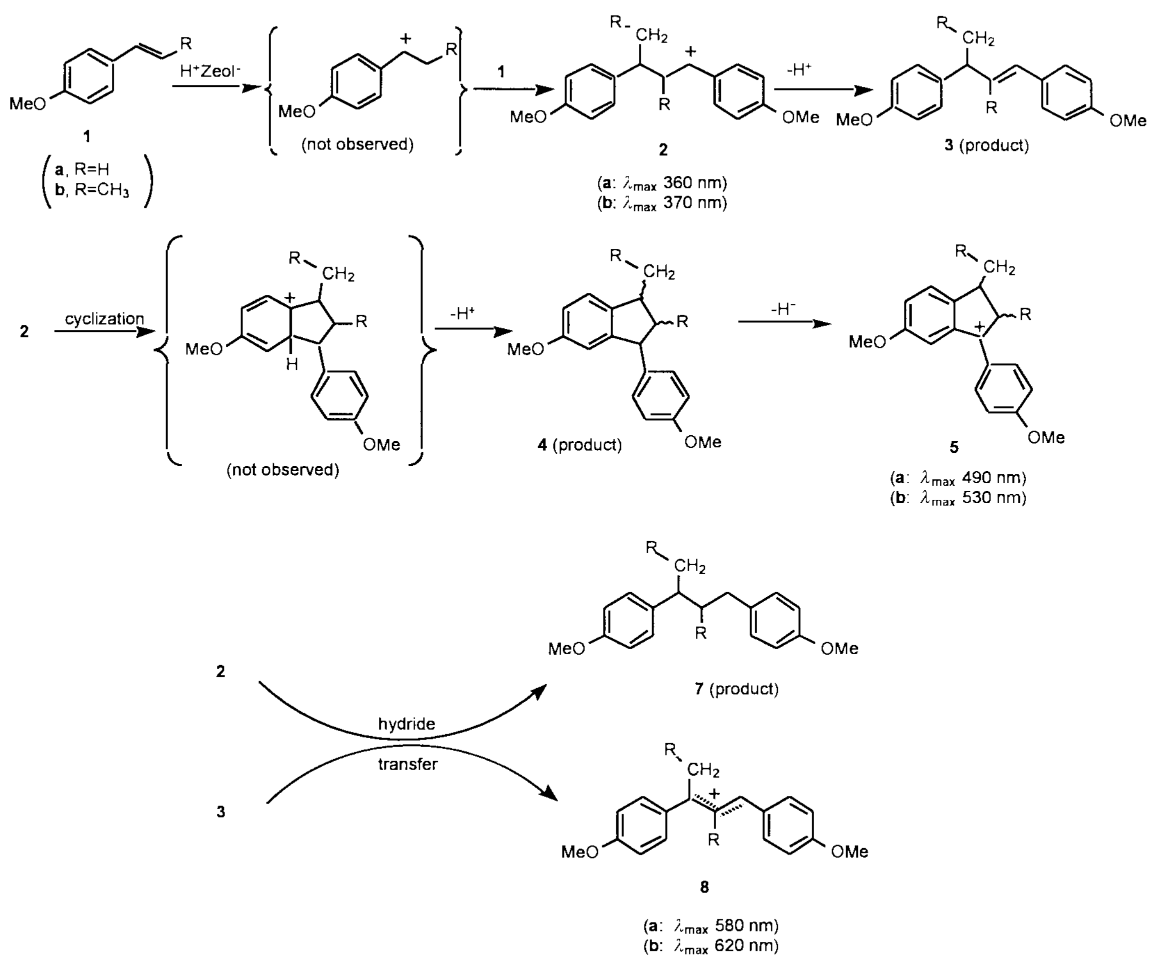


Fig. 14 Diffuse reflectance UV-vis spectrum (plotted as the inverse of the reflectance, *R*) after incorporation of 4-methoxystyrene in zeolite HBeta. The structure of the allylic cations responsible for the spectrum are shown on top of the plot. The λ_{max} predicted by semiempirical calculations is indicated in the graph (An = 4-MeOC$_6$H$_4$–).

We undertook a detailed UV-vis spectroscopic kinetic study of the reaction of 4-methoxystyrene in acid zeolites showing the formation and decay of several transients on the way to the final, persistent 1,3-bis(4-methoxyphenyl)but-2-en-1-yl cation.[52] Since the lifetime of many of the intermediates involved is on the minute time scale, this study can be conveniently carried out after incorporation of 4-methoxystyrene in acid zeolites with a conventional spectrophotometer (Fig. 16). The kinetic data is compatible with the reaction mechanism shown in Scheme 20, in which the key step in the formation of 1,3-bis(4-methoxyphenyl)but-2-en-1-yl cation is a hydride transfer between the primary linear dimer as donor and with any of the other thermodynamically less stable carbocations involved as acceptors, particularly 1-(4-methoxyphenyl)ethyl and 1,3-dianisylbut-1-yl cations.

A closely related example is the case of the dimerisation of 1,1-diphenylethylene catalysed by acid zeolites. Again, upon adsorption of this compound in zeolites the corresponding dimers derived from an acid-catalysed mechanism are formed (Scheme 21). Concomitantly, the zeolite becomes deep blue in colour exhibiting a characteristic UV-vis spectrum (Fig. 17). This species was first observed upon adsorption of diphenylethylene on amorphous silica–alumina in the context of the ability of solid acids to generate radical ions. Thus, the blue species was initially assigned to the diphenylethylene radical cation,[53,54] and later recognised to be an organic carbocation, although of uncertain structure.[55]

More recently, the same blue species has also been observed upon adsorption of 1,1-diphenylethylene in HY zeolite.[56,57] Although in one report the species was once again wrongly assigned to a radical cation,[56] our EPR measurements con-



Scheme 20 Reaction mechanism of the acid-catalysed dimerisation of vinylanisole that is compatible with the observed changes in the diffuse-reflectance UV-vis spectra of the zeolites.

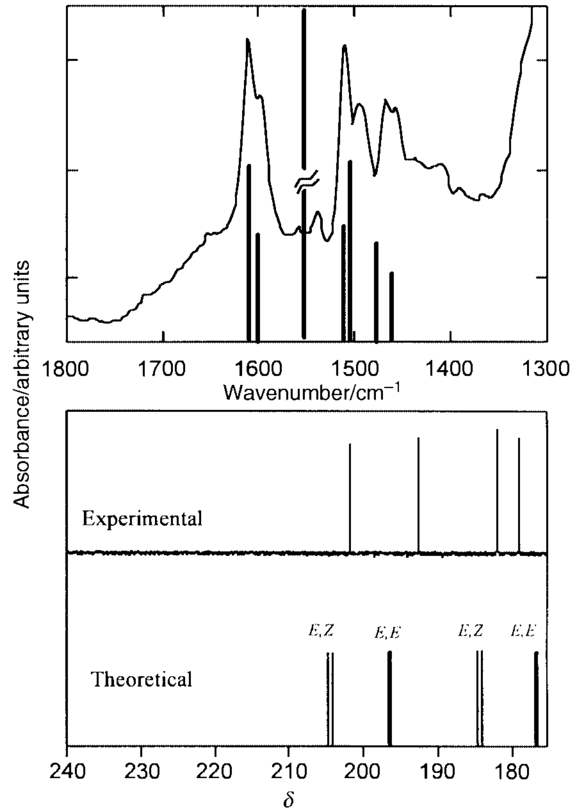


Fig. 15 Experimental IR (top) and ^{13}C NMR (bottom) spectra attributed to the 1,3-dianisylbut-2-en-1-yl cation compared to those predicted by *ab initio* calculations.

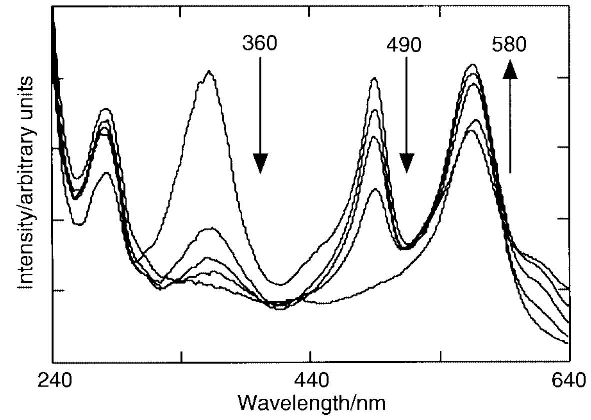


Fig. 16 Periodic diffuse-reflectance UV-vis spectra upon incorporation of vinylanisole into the HY zeolite. For the assignment of the 360, 490 and 580 nm bands see Scheme 20.

firmed earlier results on silica–alumina that the species cannot have an unpaired electron.[57] By generating the same blue species in solution, we have been able to record the ^{13}C NMR spectrum of the deep blue solutions and show that the species responsible for the intense colour is only present in trace amounts, below the detection limit of the ^{13}C NMR technique. The predominant products in the blue solution are the neutral dimers (Fig. 18A). *In situ* IR spectroscopy of the blue zeolites also points to the dimers as the major components in the organic material adsorbed within the solid (Fig. 18B).

Therefore, all the data available suggest that in the case of the 1,1-diphenylethylene, the colour and the UV-vis spectra of the solids are likely to be due to trace amounts of a thermo-

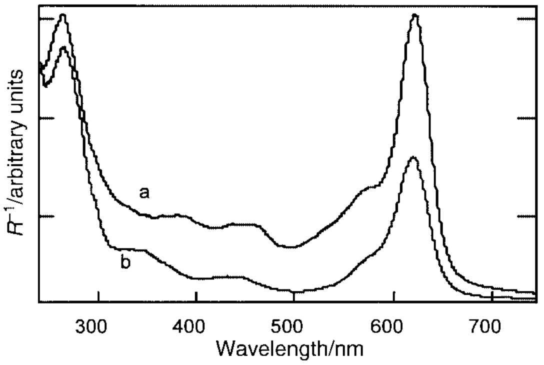


Fig. 17 Diffuse-reflectance UV-vis spectra of 1,1-diphenylethylene adsorbed on HY (a) and H-Beta (b) zeolites.

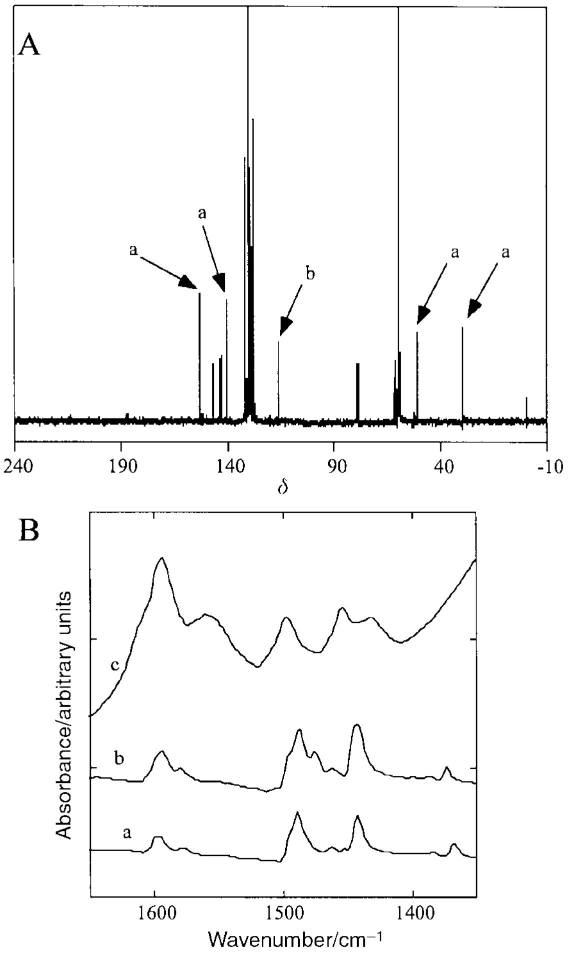
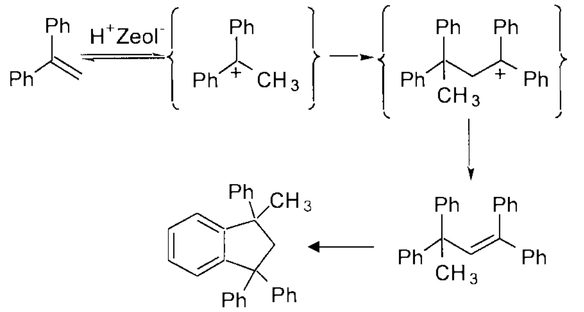
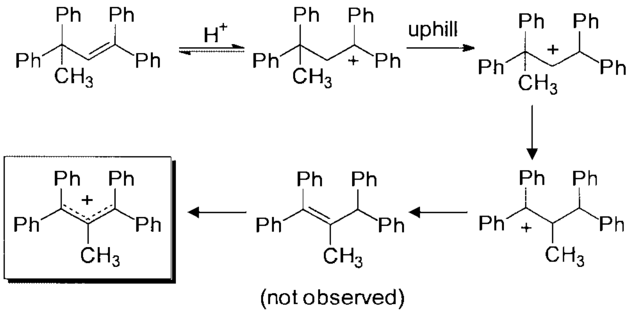


Fig. 18 A: ^{13}C NMR spectrum recorded by dissolving 1,1-diphenylethylene in dimethyl sulfate containing H_2SO_4. The characteristic carbons corresponding to the neutral 1,1,3,3-tetraphenylbut-1-ene dimer and unreacted diphenylethene have been labelled with the letters a and b, respectively. B: Aromatic region of the FT-IR spectra of the linear 1,1,3,3-tetraphenylbut-1-ene (a) and the cyclic diphenylindene dimers (b) in a KBr disk compared to the organic material present in the blue H-Beta zeolite after incorporation of 1,1-diphenylethylene (c).

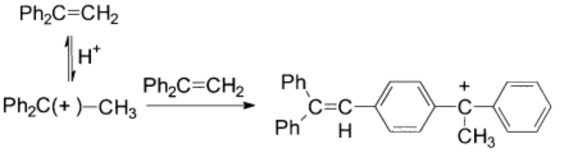
dynamically very stable carbocation. Some allylic cations have been suggested,[58] and they certainly would be compatible with the UV-vis spectrum. However, the evidence for these structures based exclusively on the limited information of the UV-vis spectroscopy is highly questionable since many other alternate conjugated structures would also be compatible with the 605 nm absorption band. Furthermore, the formation of these allylic carbocations would require at least one thermodynamically uphill rearrangement that would make the overall process unfeasible (Scheme 22). Perhaps the most reasonable proposal in this regard is that of Rooney assigning the blue species to a 1,1-diphenylethyl cation having in the *para* position of one of the phenyl rings a diphenylethenyl. This cation would arise from the *para* attack of the 1,1-diphenylethyl cation on a neutral diphenylethylene (Scheme 23).[59]



Scheme 21 Dimeric products observed in the organic phase upon incorporation of 1,1-diphenylethylene in acid zeolites.



Scheme 22 Proposed structure of the tetraphenyl-substituted allyl cation responsible for the blue species (605 nm) formed upon adsorption of diphenylethylene in acid zeolites. Note that the second step (hydride migration) is unfavorable by as much as 31 kcal mol^{-1} and that a predicted product is not observed.



Scheme 23 Proposed structure and formation mechanisms for the blue species derived from 1,1-diphenylethylene according to ref. 59.

Concluding remarks

Zeolites are widely used in heterogeneous catalysis and as compartmentalised hosts to incorporate reactive organic intermediates. While at the present these two fields appear essentially as independent with totally different interests, what we hope to have shown through some selected examples is that they share a common rationale in the nature of the species that are retained inside and desorbed out of the pores. Certainly the structure of the species adsorbed in the solid and the products present in the liquid phase have to be different with totally opposed affinities, but their mechanism of formation from the substrates have common pathways. Since we have frequently found that the organic material adsorbed within the pores after a catalytic reaction forms a single, pure species, these type of studies are relevant in the context of the preparation of new hybrid materials with special photochemical, optical, magnetic and catalytic properties.

Acknowledgements

We would like to express our deepest gratitude to all our coworkers and colleagues that have contributed over the years with their effort and thinking to these studies. Generous financial support by the Spanish DGICYT (Grants PB93-0380 and MAT97-1060-CO2) is gratefully acknowledged.

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