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Anionic Organic Guests Incorporated in Zeolites: Adsorption and Reactivity of a Meisenheimer Complex in Faujasites

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Abstract: Zeolites are suitable microporous hosts for positively charged organic species, but it is believed that they cannot adsorb organic anions. Pure Meisenheimer complex, derived from reduction of 2,4-dinitroaniline with $NaBH_4$, was adsorbed inside faujasite cavities. Evidence for the internal incorporation of this negatively charged reaction intermediate comes from 1) XPS elemental analysis as a function of the depth of penetration into the particle, 2) the remarkable blue shift in λ_{max} of the Meisenheimer complex adsorbed on zeolite (ca. 470 nm) as compared to that in acetonitrile (580 nm) and 3) from the lack of reactivity with size-excluded hydride-acceptor reagents. Evidence is provided in support of an adsorption mechanism in which a neutral ion pair (alkali metal ion+Meisenheimer anion) is the actual species being adsorbed. In fact it appears that there is remarkable increase in the association constant for the ion-pair complex within the zeolite cavities as compared to DMF solution. Although this mechanism of adsorption as an ion-pair complex has precedents in the adsorption of some inorganic salts, what is novel is the notable increase in the stability and persistence of the Meisenheimer anion (a anionic reaction intermediate) as a result of zeolite inclusion. Adsorbed Meisenheimer complex exhibits much lower reactivity towards electron acceptors, oxygen, and water. Cyclic voltammetry of zeolite-modified electrodes reveals for the Meisenheimer complex adsorbed on LiY a reversible redox peak that is not observed in solution and has been interpreted as arising from site isolation and stabilisation of the electrochemically generated species.

Keywords: alkali metals • host–guest systems • ion pairs • reactive intermediates • zeolites

Introduction

Zeolites have been widely used as rigid matrices to host elusive positively charged organic reaction intermediates.[1,2] Particularly remarkable effects have been reported when positively charged species tightly fit into the pores defined by the rigid aluminosilicate framework. In these cases, the zeolite guest becomes stabilised by the intense electrostatic fields experienced inside the pores and by the effective protection of the zeolite walls against attack of nucleophilic reagents.[3]

Thus, the lifetime of photochemically generated radical cations increases by up to six orders of magnitude as compared to organic solvents when they are generated inside zeolites.[4,5] Besides stabilisation of transient intermediates, it has also been observed that some organic cations and radical cations became indefinitely persistent when they are encapsulated in appropriate zeolites.[6–16]

In contrast to the wealth of information regarding the behaviour of positively charged ions, little work has dealt with the incorporation of negatively charged organic species in zeolite micropores.[2] The reason for this paucity is that the negatively charged zeolite frameworks are more suited to including positively charged and neutral species, while access of negatively charged organic molecules to the interior of the pores is impeded. The main reason for the lack of intraparticle anion diffusion is that Coulombic repulsion be-

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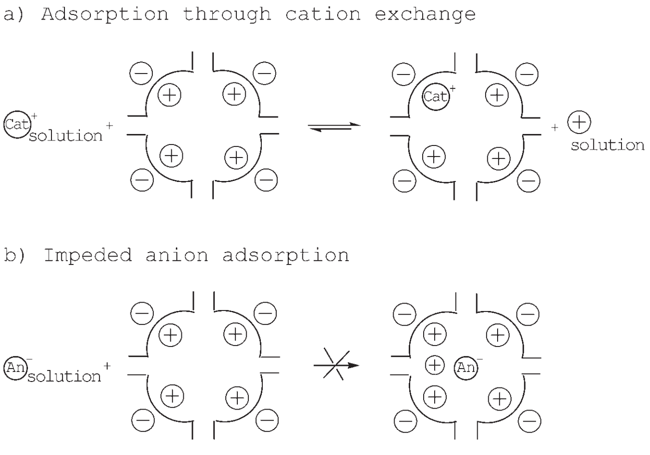
tween anions and the negative zeolite framework causes an electrostatic barrier that blocks the entrance of the anions into the pores. On the other hand, zeolites can adsorb cations by an ion-exchange mechanism in which internal charge-balancing cations located close to the framework negative charges migrate to the exterior of the zeolite particle simultaneously with the ingress of another cation to replace the original one. In each moment of cation exchange, electroneutrality of the solid is maintained (Scheme 1 a). This cation-exchange mechanism cannot operate for the incorporation of anions.



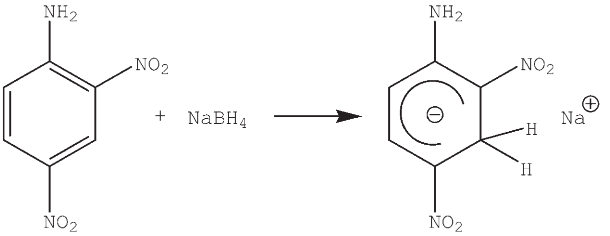
Scheme 1.

Thus, zeolites are well known cation-exchange solids, but the ingress of significant amounts of anions is commonly considered much more difficult and disregarded (Scheme 1 b). Clearly if the ingress of an anion into a zeolite were possible, it should be accompanied by the corresponding charge-balancing cation to maintain the electroneutrality of the solid. Only scarce precedents have described the presence of inorganic anions in zeolites.[17,18] For instance, CN^- was adsorbed to form $[Co(CN)_5]^{2-}$ in zeolite Y cages,[19,20] and I^- has been demonstrated to be easily adsorbed[21–23] and even form charge-transfer complexes with incorporated viologen.[24] Manganate carbonyl salts have been used to induce thermal electron transfer in zeolite micropores.[25] This adsorption of inorganic anions has been referred to as "salt occlusion". In some other cases, the internal anion is generated in situ from a neutral precursor, examples of which are limited to a few species including superoxide,[26] polysulfide and polyselenide radical anions,[27] iodide,[28] fullerene[29,30] and aromatic hydrocarbon radical anions.[31–35] Given the increasing importance of zeolites as rigid hosts defining a compartmentalised space in which chemical reactions can be controlled and altered with respect to solution and in which multicomponent systems can be assembled,[36] it is of interest to expand the current knowledge about stabilisation and reactivity of positively charged guests to negatively charged organic species. To open this field, it is necessary to demonstrate that carbanions can be incorporated in zeolites, particularly considering that carbanions are reaction intermediates that are destroyed by acidic OH groups such as those of silanols. Then, it would be of interest to determine what effects on anion stability and reactivity are derived from the host–guest interaction with zeolites.

Here we report the successful adsorption of a negatively charged Meisenheimer complex in the internal pores of zeolites and the remarkably reactivity changes that result upon their incorporation. Meisenheimer complexes are important reaction intermediates formed by the attack of negatively charged nucleophiles on electron-poor benzene derivatives.[37–43] Fundamental studies on the structure and reactivity of Meisenheimer complexes have rationalised the regioselectivity of nucleophilic aromatic substitution.[37] The reactivity of these intermediates is also relevant in the context of biological reductions with NADH, which can be considered to be a Meisenheimer adduct of nicotinamide. Our study on the incorporation of negatively charged Meisenheimer complexes in zeolites demonstrates that the methodology to study elusive species by adsorbing organic reaction intermediates inside zeolites can also be expanded to organic anions and opens a new area in intrazeolite chemistry. Here we show that a negatively charged Meisenheimer complex included in zeolites with high framework Al contents becomes remarkably stabilised and considerably less reactive than the same species in solution. Evidence is provided that this unexpected stabilisation arises from unprecedented association with alkali metal cations, which is also observed in polar solvents but with much lower strength.

Results and Discussion

Incorporation of the Meisenheimer complex into Na^+ zeolites: We prepared pure Meisenheimer complex in anhydrous acetonitrile starting from 2,4-dinitroaniline by reaction with sodium borohydride [Eq. (1)]. The resulting



(1)

sodium salt of the Meisenheimer complex was purified by crystallisation and fully characterised spectroscopically. Particularly important in assessing the purity of our Meisenheimer sample was the ^1H NMR spectrum, in which formation of the Meisenheimer complex from 2,4-dinitroaniline produces significant changes in the chemical shift of the two doublets corresponding to H-5 and H-6 of the aromatic ring from $\delta = 8.16$ and 7.11 ppm in the aromatic compound to $\delta = 7.43$ and 5.10 ppm, respectively, accompanied by the appearance of a singlet due to a methylene group at $\delta = 3.57$ ppm. Also the ^{13}C NMR spectrum agrees completely with the structure of the σ complex formed by hydride attack at the 3-position of 2,4-dinitroaniline.[44–46] In addition to NMR spectroscopy, the Meisenheimer complex in acetonitrile solution exhibits a characteristic UV/Vis absorption band at 578 nm that can be used to identify unambiguously its presence in mixtures containing neutral 2,4-dinitroaniline ($\lambda_{max} = 333$ nm). All these data are in agreement with those reported in the literature.[45] Thus, according to NMR spectroscopic data we are adsorbing into the zeolite a solution of the sodium salt of pure Meisenheimer complex, and no other species, particularly 2,4-dinitroaniline, could be observed during adsorption.

Crystals of the Meisenheimer complex were dissolved in anhydrous acetonitrile, and adsorption was attempted in a series of crystalline (zeolites) and amorphous silicates. Considering the negative charge of the Meisenheimer complex, one would have anticipated that no adsorption of this intermediate in the zeolites would take place. Nevertheless, significant amounts of the Meisenheimer complex were adsorbed on sodium faujasites, as indicated by diffuse-reflectance UV/Vis spectra of these solids. Figure 1 shows the diffuse-reflectance UV/Vis spectrum of dry powders of NaY after contacting dehydrated NaY samples with anhydrous acetonitrile solutions of the sodium salt of the Meisenheimer complex.

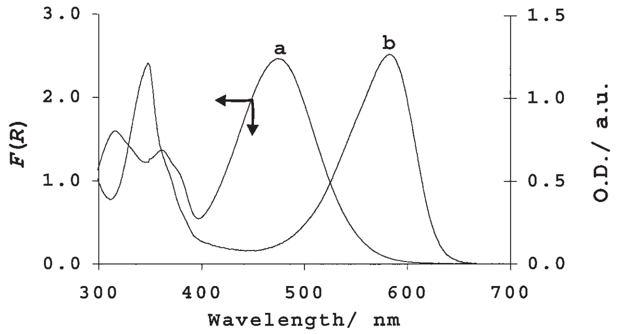
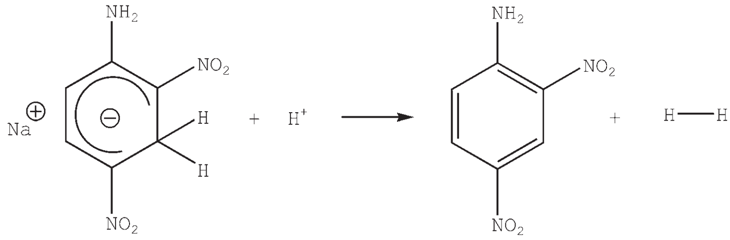


Figure 1. Diffuse-reflectance UV/Vis spectra recorded a) as the Kubelka–Munk function of the reflectance $F(R)$ and b) as the O.D. of the solution for samples of Meisenheimer complex adsorbed on NaY (a) or in 10^{-3} M acetonitrile solution (b).

When adsorption was attempted for an acid zeolite in the protic form or with zeolites having a large population of silanol groups, the Meisenheimer complex was immediately destroyed and the corresponding diffuse-reflectance UV/Vis spectra showed the absence of this reaction intermediate. This was the case for an H$^+$-Beta zeolite or an all-silica Beta with a large population of silanol groups. This behaviour is in agreement with the known reactivity of the Meisenheimer complex, which is readily attacked by protons and acidic hydroxy groups [Eq. (2)].[40,41,43,44]



(2)

In contrast to the behaviour of these H$^+$-Beta and all-silica Beta zeolites, it is known that highly crystalline faujasites, either X or Y, have a strongly reduced population of silanol groups. Figure 2 shows the OH region of the IR spectra of the zeolites used in these experiments to illustrate the remarkable variations in the silanol density of the solids. Silanol groups (p$K_a \approx 6$) must be acidic enough to destroy the Meisenheimer complex by protonation [Eq. (2)]. As can be seen in Figure 2, our NaX and NaY zeolites are almost devoid of surface silanol groups. On the other hand, the amount of Meisenheimer complex adsorbed, as assessed by combustion chemical analysis, is significantly higher in NaY (0.51 wt% C) than NaX (0.36 wt% C). This can be rationalised by the larger free micropore volume of NaY as compared to NaX and/or to the lower electrostatic barrier against diffusion of negative ions in zeolite NaY as compared to zeolite NaX, since the framework negative charge of zeolite NaY (Si/Al 2.4) is about one-half of that of zeolite NaX (Si/Al 1.2). The density of negative framework charges

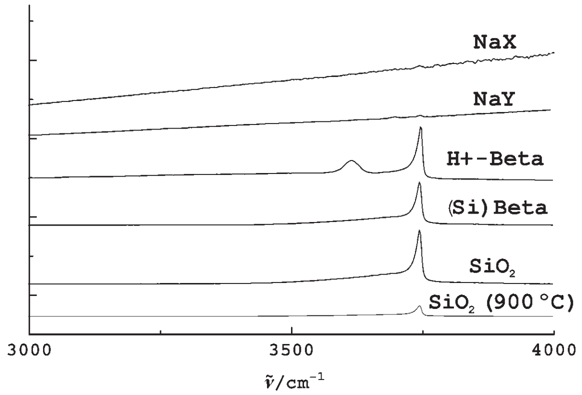
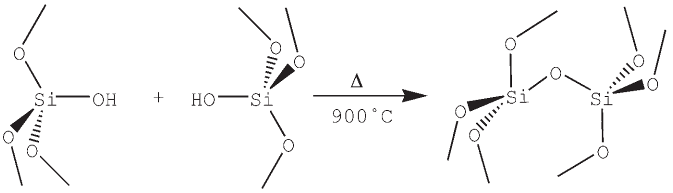


Figure 2. High-frequency region of the IR spectra recorded at room temperature in sealed cells for a series of zeolites (10 mg, self-supported wafers) after outgassing the co-adsorbed water at 200 °C under 10^{-2} Pa for 1 h. The presence of SiOH groups is revealed by the characteristic stretching band at 3720 cm^{-1}, while acidic Si(OH)Al hydroxy bridges appear as a broader band at 3600 $^{\text{cm}-1}$. Note that our dehydrated NaX and NaY faujasites are almost free of hydroxy groups according to IR spectroscopy.

is related to the framework Al content of the zeolites, since each AlO_4^{5-} tetrahedra introduces a net negative charge in the aluminosilicate wall and is associated with a charge-balancing cation.

When assessing the role of zeolite microporosity on the adsorption and its influence on the chemical reactivity of presumably incorporated organic guests, a good test is to compare the behaviour of microporous zeolites with that of amorphous silica and silica-alumina (25% Al_2O_3). These two inorganic oxides have a chemical composition akin to that of zeolites, but they lack the crystal structure and pore system of zeolites. In other words, amorphous silicas are not microporous. In the case considered here, the Meisenheimer complex could not be characterised by conventional spectroscopy as a persistent species to the ambient atmosphere on the external surface of silica and silica-alumina, irrespective of whether the silica-alumina was in its acid or Na^+ form. Diffuse-reflectance UV/Vis spectroscopy clearly demonstrates the absence of Meisenheimer complex on amorphous SiO_2 or SiO_2–Al_2O_3 after performing adsorption from anhydrous acetonitrile solutions of pure Meisenheimer complex under the same conditions as for zeolites and exposing the solids to the ambient environment. The only compound that could be identified on the surface of silica and silica-alumina after attempted adsorption of Meisenheimer complex was 2,4-dinitroaniline, which was fully characterised by ^1H NMR spectroscopy after extracting the amorphous solids. Moreover, the loading of 2,4-dinitroaniline determined by combustion chemical analysis of the silica and silica-alumina solids was 2.5 wt%, and this rules out that the failure to detect the Meisenheimer complex on silica and silica-alumina was due to the failure to adsorb organic species on their external surface. Thus, the behaviour of silica and silica-alumina can be interpreted as indicating that in nonporous silica and silica-alumina solids, the Meisenheimer complex adsorbed on the external solid surface does not survive exposure to the atmosphere long enough to permit recording a diffuse-reflectance UV/Vis spectrum. Apparently, the Meisenheimer complex is rapidly attacked by moisture, oxygen or surface silanol groups and is promptly converted to 2,4-dinitroaniline.

To address the influence of the density of silica silanol groups on the stability of the Meisenheimer complex, a special SiO_2 sample calcined at 900°C was also used. It is known that the population of silica silanol groups can be minimised by calcination of the sample at high temperatures, due to thermally induced condensation of neighbouring silanol groups to form silanoxy bridges [Eq. (3)].[47–50] However, even with this special surface-dehydroxylated SiO_2 sample (see Figure 2 for its relative silanol population), no stabilisation of Meisenheimer complex was observed, while chemical analysis indicated that the adsorption of Meisenheimer complex is somewhat enhanced (5 wt%) with respect to uncalcined SiO_2 samples. This result seems to indicate attack of atmospheric agents as the main process responsible for the disappearance of Meisenheimer complex on the surface of nonmicroporous SiO_2 or SiO_2–Al_2O_3 rather than the presence of silanol groups in the solids.



(3)

The lack of persistence of the Meisenheimer complex on silica or silica-alumina compared to faujasites can be readily interpreted as reflecting the positive influence on the stability of the Meisenheimer complex of its inclusion within the micropores. Samples of Meisenheimer-containing NaY and NaX zeolites stored in capped vials under air do not undergo any visible aging over periods longer than three months. In contrast, pure crystals of Meisenheimer complex are also rapidly attacked under identical storage conditions in a few hours.

In addition to the direct adsorption of Meisenheimer complex from preformed solutions, we also attempted in situ formation of Meisenheimer complex by adsorption of neutral 2,4-dinitroaniline and reaction with an excess of $NaBH_4$. Surprisingly, 2,4-dinitroaniline (10^{-2} M) could not be adsorbed on sodium faujasites. The ability of zeolites to adsorb organic guests inside the pores, provided that their molecular size is smaller than the pore openings, is well documented.[17,18,51] Thus, the failure to adsorb 2,4-dinitroaniline was unexpected in view of its small kinetic diameter. To explain this result we studied the influence of 2,4-dinitroaniline concentration on its optical spectra with the aim of obtaining some spectroscopic evidence for the formation of 2,4-dinitroaniline aggregates. The large dipole moment of 2,4-dinitroaniline, the presence of strong electron-withdrawing and electron-donor substituents and the possibility of hydrogen-bond formation will promote the strong association of these molecules. Aggregation of the molecules would increase the size of the diffusing entity and impede diffusion into the micropores.

To check for possible 2,4-dinitroaniline aggregation, we recorded its UV/Vis spectrum in acetonitrile at different concentrations in the range of those used for adsorption. On dilution, the band at the longest wavelength (λ_{max} between 427 and 400 nm) gradually shifts to shorter wavelengths and decreases in intensity until it becomes a shoulder and eventually disappears (Figure 3).

We attribute this 400–427 nm band to the presence of 2,4-dinitroaniline aggregates and its variation in λ_{max} and intensity as reflecting changes in the degree and strength of aggregation as well as in the aggregate concentration on dilution of the monomer. In fact, by working in CH_3CN at dilute concentrations of 4.7×10^{-4} M we were able to adsorb on sodium faujasites an amount of 2,4-dinitroaniline large enough to be detected by UV/Vis spectroscopy, while incorporation at higher concentration ($>10^{-3}$ M) was unsuccessful. Formation of 2,4-dinitroaniline aggregates can also be inferred from small but significant chemical shift variations of

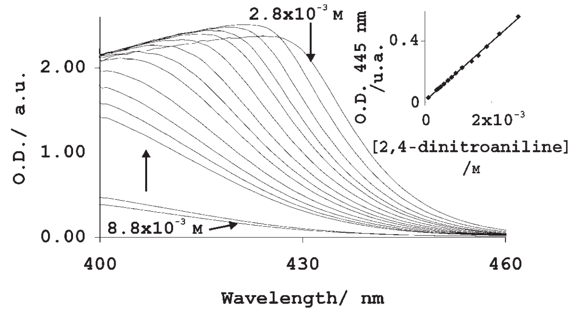


Figure 3. Transmission UV/Vis spectra of a solution of 2,4-dinitroaniline in acetonitrile with gradually decreasing concentration in the range from 2.8×10^{-3} to 8.8×10^{-5} M. The inset shows the plot of the O.D. measured at 445 nm versus the concentration of 2,4-dinitroaniline.

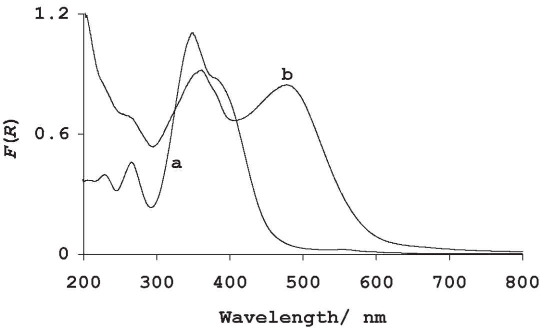
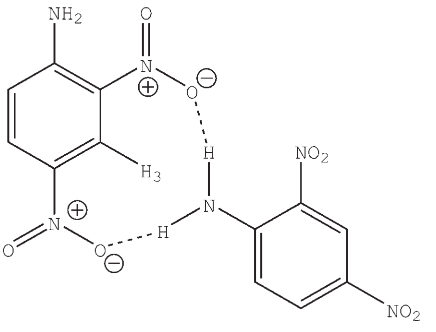


Figure 4. Diffuse-reflectance UV/Vis spectra of 2,4-dinitroaniline adsorbed on NaBeta before (a) and after (b) treatment with an acetonitrile solution of $NaBH_4$. Spectrum b corresponds to that of the Meisenheimer complex and indicates the success of hydride reduction.

H-3, H-5 and H-6 in the ^1H NMR spectrum as a function of the concentration at which the spectrum is recorded. The fact that H-5 and H-6 undergo minor variations in their chemical shifts (ca. 0.004 ppm on aggregation) while the shift for H-3 is more pronounced (ca. 0.012 ppm) gives valuable information about the structure of the aggregates. A molecular model for a dimer compatible with ^1H NMR data (Scheme 2) shows formation of hydrogen bonds between the amino and the two aromatic nitro groups.



Scheme 2.

After incorporation of 2,4-dinitroaniline in sodium faujasites from 4.7×10^{-4} M solutions in CH_3CN, the Meisenheimer complex was generated in situ by treatment with an excess of $NaBH_4$ in acetonitrile. The success of in situ generation of Meisenheimer complex was assessed by diffuse-reflectance UV/Vis spectroscopy. Figure 4 shows the optical spectra of an Na Beta zeolite containing pre-adsorbed 2,4-dinitroaniline before and after reaction with $NaBH_4$. The behaviour and properties of the in situ generated samples were identical to those prepared by adsorption of preformed Meisenheimer complex.

UV/Vis spectroscopic study on the adsorbed Meisenheimer complex: Successful incorporation of Meisenheimer complex in the micropores of NaX and NaY faujasites as persistent guests is immediatly reflected in the solvatochromic shift observed in its characteristic optical spectrum. In anhydrous acetonitrile, the Meisenheimer complex exhibits a visible band at 578 nm (Figure 1 b), responsible for its intense purple colour. In contrast, after zeolite adsorption, the diffuse-reflectance UV/Vis spectra recorded for the dry powders exhibit a remarkable blue shift of λ_{max} of about 100 nm with respect to λ_{max} in acetonitrile.

To understand the origin of this dramatic solvatochromic shift, we performed a series of measurements in solution in which the optical spectrum of the Meisenheimer complex was recorded in anhydrous DMF solutions in the presence of increasing concentrations of alkali metal salts. DMF is a more suitable solvent for this study than acetonitrile due to the higher solubility of ionic compounds in DMF. Figures 5–9 show some representative optical spectra recorded at different concentrations of alkali metal ions. In the case of K^+ and Cs^+ (Figures 7 and 8) no significant shifts in λ_{max} were observed in the absorption spectrum with increasing concentration. In contrast, in the case of Na^+ and Li^+ (Figures 5 and 6), the UV/Vis spectrum of the Meisenheimer complex in anhydrous DMF exhibits gradual shifts in λ_{max} towards shorter wavelengths together with an apparent decrease in the molar absorption coefficient with increasing concentration of these alkali metal cations.

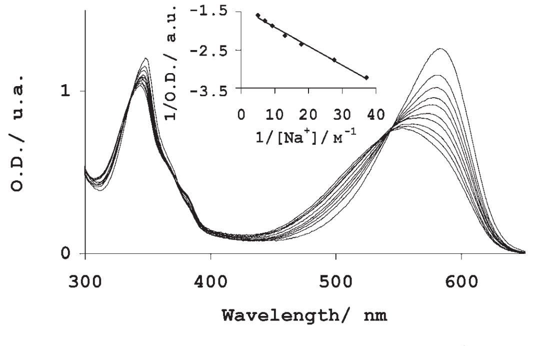


Figure 5. Transmission UV/Vis spectra recorded for a 10^{-3} M solution of the Meisenheimer complex in anhydrous DMF in the presence of $NaClO_4$ from 0 to 0.2 M. The insert shows 1/O.D. measured at 578 nm plotted against 1/[Na^+], from which the association constant of the Meisenheimer/Na^+ complex in DMF can be deduced. The magnitude of O.D. in the Benessi–Hildebrand plot of the inset is the difference in O.D. of the absortion band with and without $NaClO_4$.

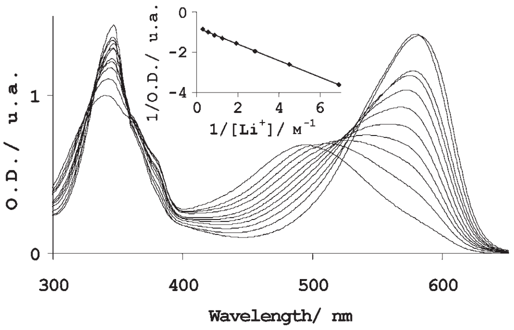


Figure 6. Transmission UV/Vis spectra recorded for a 10^{-3} M solution of the Meisenheimer complex in anhydrous DMF in the LiCl from 0 to 3.4 M. The inset shows 1/O.D. measured at 578 nm plotted against 1/[Li^+], from which the association constant of the Meisenheimer/Li^+ complex in DMF can be deduced. The magnitude of O.D. in the Benessi–Hildebrand plot of the inset is the difference in O.D. of the absorption band with and without LiCl.

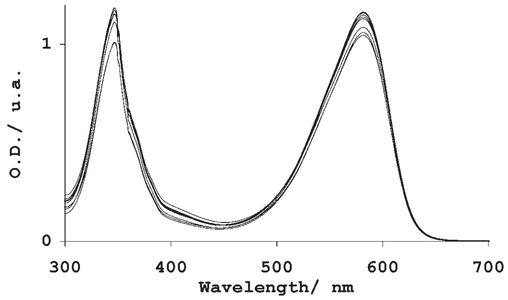


Figure 7. Transmission UV/Vis spectra recorded for a 10^{-3} M solution of the Meisenheimer complex in anhydrous DMF in the presence of increasing concentration of K_2SO_4 from 0 to 0.1 M. The latter concentration corresponds to the saturation concentration at room temperature of the salt in DMF.

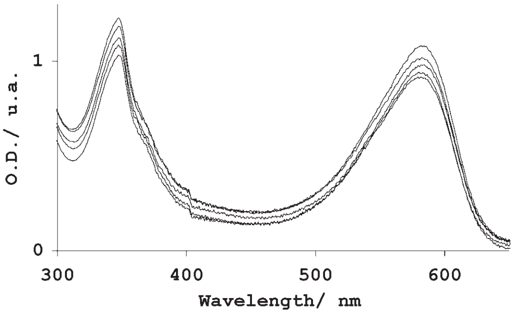


Figure 8. Transmission UV/Vis spectra recorded for a 10^{-3} M solution of the Meisenheimer complex in anhydrous DMF in the presence of increasing concentration of $CsCH_3CO_2$ from 0 to 0.1 M.

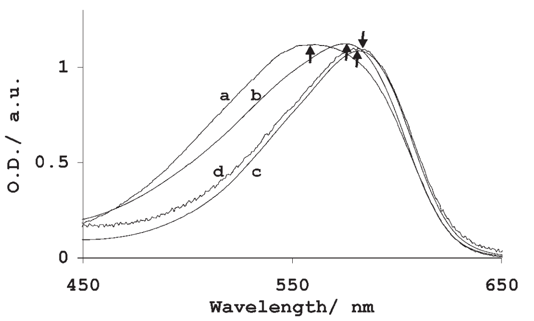
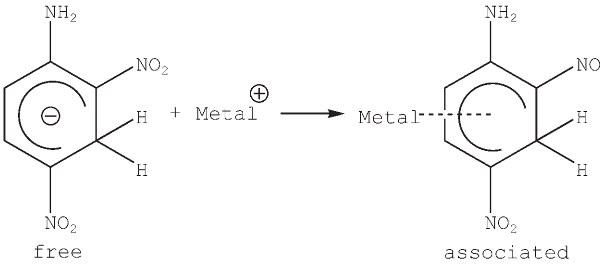


Figure 9. Comparison of the characteristic visible absorption band of the Meisenheimer complex measured for 0.1 M DMF solutions of the different alkali metal cations employed: a) Li^+, b) Na^+, c) K^+, and d) Cs^+. The arrows indicate the λ_{max} of each band.

The above observations on the influence of the nature and concentration of alkali metal ions on the optical spectrum in solution can be rationalised by assuming that in anhydrous DMF the Meisenheimer complex at millimolar concentration is present mostly as dissociated free ions with an absorption band around 578 nm. These ions can associate with Li^+ or Na^+ as counterions to form an ion pair whose absorption λ_{max} shifts to shorter wavelengths [Eq. (4)]. Superimposed on this Coulombic Meisenheimer/alkali metal ion association there may also be a solvatochromic effect as



(4)

a function of the ionic strength and polarity of the medium that affects basically the λ_{max} of the ion pair (note that there is a gradual red shift in λ_{max} of the associated ion pairs) but does not affect that of the free Meisenheimer ion (note that in Figure 5 and Figure 6, λ_{max} at 578 nm attributable to the free Meisenheimer complex remains unvaried). This solvatochromic shift of λ_{max} for the associated Meisenheimer-alkali metal ion pair explains the absence of clear isosbestic points between the bands at 578 and about 480 nm, particularly for Li^+ (Figure 6), for which higher salt concentrations can be obtained in DMF. However, two clear isosbestic points at much shorter wavelengths (330 and 370 nm) indicate changes also in this UV region of the spectrum and interconversion between two species. Assuming a 1/1 stoichiometry for the Meisenheimer/alkali metal ion complex and by applying the Benessi–Hildebrand equation, the association constant in DMF for the Li^+/Meisenheimer complex was estimated to be 1.88 M. The range of concentrations available in DMF for Na^+ salts was too low to obtain an accurate value of the association constant for the Na^+/Meisenheimer complex, although it is clearly lower than that of the Li^+ complex, in agreement with the variation in the charge density from Na^+ to Li^+. K^+ and Cs^+ do not form complexes to a measurable extent. As far as we know the formation of these ion pairs between Meisenheimer complexes and alkali metal ions has not been reported.

The behaviour of the Meisenheimer complex in anhydrous DMF solution can serve as basis to understand the remarkable shift in $\lambda_{\max}$ (ca. 100 nm) observed on absorption of Meisenheimer complex in zeolites. By comparing $\lambda_{\max}$ in zeolites with those recorded in anhydrous DMF solution it can be concluded that incorporation in sodium faujasites produces a similar effect to that observed in solution for high Na^+ concentrations but of considerably stronger intensity, as judged by the shift in $\lambda_{\max}$. For instance, in $NaClO_4$-saturated, anhydrous DMF (0.2 M) $\lambda_{\max}$ of the ion pair appears at 515 nm. Analogously, for LiCl-saturated, anhydrous DMF (3.4 M) the –Meisenheimer/Li^+ complex has $\lambda_{\max}$ at 495 nm. The same effect, albeit considerably stronger, could be responsible for the fact that in faujasites NaX and NaY the observed $\lambda_{\max}$ is 444 and 471 nm, respectively. In this regard, extrapolation of the solution data indicates that incorporation of the Meisenheimer complex into NaY would be equivalent to a 5 M solution of NaCl in DMF.

To demonstrate that also inside zeolites there is an influence of the nature of the alkali metal ion, we prepared LiY and studied the incorporation of the Meisenheimer complex in this zeolite. The Meisenheimer complex adsorbed on LiY exhibits $\lambda_{\max}$ at 457 nm (cf. $\lambda_{\max}=471$ nm for NaY), and this again reflects the stronger association constant of Li^+ with respect to Na^+.

Evidence in support of the internal location of the adsorbed Meisenheimer complex: The above variation in $\lambda_{\max}$ values suggests that the Meisenheimer complex is strongly associated with the charge-compensating alkali metal ions present in the zeolite cavities and that the association constant of the Meisenheimer/Na^+ ion pair is much stronger for zeolites than in solution. This dramatic enhancement of the association constant of the Meisenheimer complex together with the internal location of the alkali metal ions is indirect evidence in support of its incorporation inside zeolite cages. An increase in the association constant of charge-transfer (CT) complexes assembled within zeolites is not unprecedented for neutral guests. Kochi coined the term “internal pressure effect” for this increase in the association constants for CT complexes between neutral arenes and viologens on encapsulation in zeolite micropores.[52–54] The influence of the nature of the alkali metal ion of the zeolite on the internal pressure effect experienced by CT complexes within faujasites has also been established by us.[55] In a certain way, confinement inside in zeolites cavities favours the interaction between CT donor–acceptor complexes by spatial confinement, which promotes proximity between the partners of the complex in a manner resembling that by which high pressures promote association in solution due to the reduction of the molecular volume on complex formation.

The remarkable shift in $\lambda_{\max}$ of the Meisenheimer complex (>100 nm) in the sense observed in solution for high alkali metal ion concentrations together with the lack of persistence of the Meisenheimer complex when adsorbed on SiO_2 (even after dehydroxylation by calcination) or SiO_2–Al_2O_3 (including its Na^+ form) are evidence in support of the location of the Meisenheimer complex inside the zeolite micropores. This assumption is also compatible with the reactivity pattern of the zeolite-bound Meisenheimer complex (see below). In fact, while spectroscopy can identify the structure of the adsorbed guest, its location cannot be determined directly by any spectroscopic technique, and it is normally inferred from indirect evidence such as abnormal spectroscopic variations or unusual reactivity.[2]

To address specifically the internal versus external location of the Meisenheimer complex we performed XPS analysis combined with fast Ar^+ sputtering. Quantitative XPS analysis gives the atomic ratio of the elements present in a very shallow (ca. 10 Å) layer of the zeolite particle. Fast-ion bombardment partially destroys the outermost surface and exposes a new surface that was originally internal. By coupling XPS analysis with fast-ion bombardment a profile of the atomic ratio versus the depth of penetration in the particle can be obtained. The results for Meisenheimer complex adsorbed on NaY samples (Figure 10) show that C and N atoms are present on the external surface but also in the interior of the particles. In fact, although the actual N/Si atomic ratio decreases with increasing depth of penetration inside the zeolite particles, nitrogen is still clearly present up to 150 Å below the external surface. This corresponds to about 10 supercages inside the zeolite particle, the maximum penetration that we were able to achieve with our fast-ion bombardment setup. Clearly, these 150 Å represent only the outermost layer of a zeolite NaY particle (particle size 10000 Å). Note that for these XPS measurements the incorporation of the Meisenheimer complex on NaY was carried out from CH_2Cl_2 solutions that were subsequently exhaustively evacuated. Therefore, the presence of N is ascribed exclusively to the Meisenheimer complex and not to the presence of residual solvent. Thus, the N/Si atomic ratio profile of Figure 10 really corresponds to the mapping of the Meisenheimer complex and is not disguised by the presence of some residual solvent. A control experiment submitting NaY to the same experimental procedure in the absence of Meisenheimer complex did not lead to the presence of N atoms. Moreover, the C/N atomic ratio of 2:1 is steady

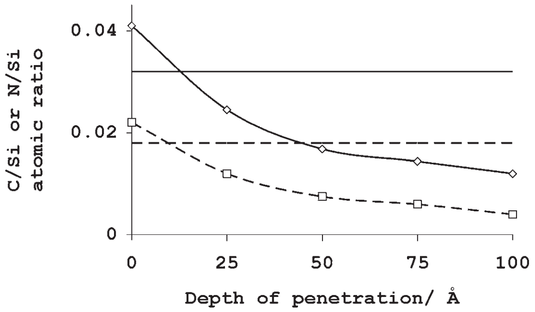


Figure 10. Depth profile of the C/Si (◇) and N/Si (□) atomic ratios obtained by XPS analysis and Ar^+ sputtering for the Meisenheimer complex adsorbed on NaY. The horizontal lines correspond to the average C/Si and N/Si atomic ratios estimated by combustion chemical analyses.

throughout the profile and corresponds to that expected for the Meisenheimer complex of 2,4-dinitroaniline. Assuming that C and N are due to the Meisenheimer complex, the N/Si profile shown in Figure 10 indicates that this species is distributed on the external and internal surface. Furthermore, Figure 10 shows the average N/Si and C/Si atomic ratios estimated from the combustion chemical analysis of the whole sample. This average is intermediate between the external and internal values, albeit closer to the external atomic ratio. This indicates that the sample has a distribution of Meisenheimer complexes in different locations, whereby externally located species predominate and contribute about 60 % to the total Meisenheimer complex present in the particle. Importantly, however, a substancial population of Meisenheimer complex is still located deep inside the particle.

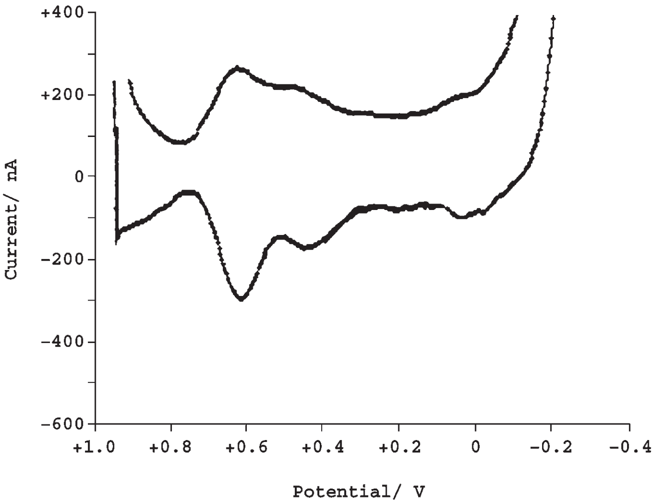
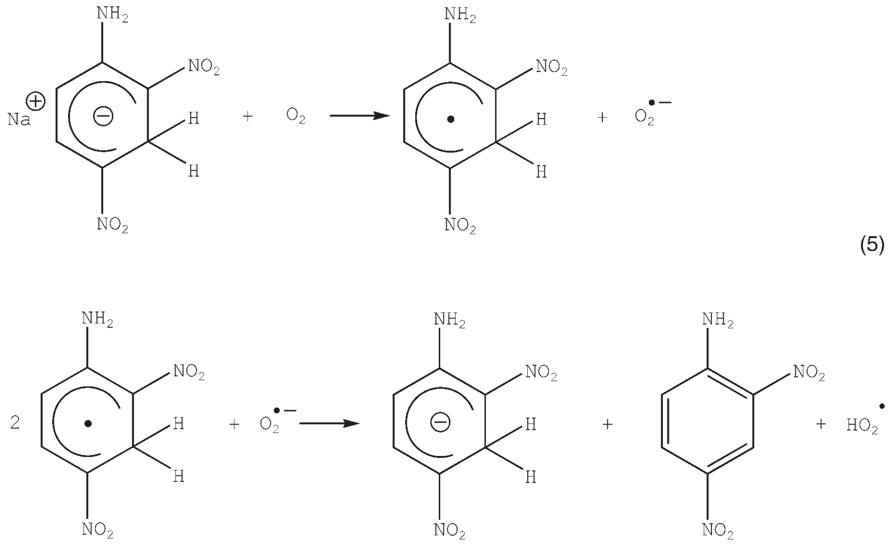


Figure 11. Semiderivative convolution of square-wave voltammograms for Meisenheimer-LiX-modified electrodes immersed in 0.10 M Et_4NClO_4/MeCN with forced electrolyte renewal. In this figure the forward, backward and total currents are represented as a function of the applied potential. Potential step increment 4 mV; square-wave amplitude 25 mV; frequency 15 Hz.

Electrochemistry of electrodes modified with NaY and LiY incorporating Meisenheimer complex also provides support to the internal location of the Meisenheimer complex. The electrochemistry of Meisenheimer complexes in solution has been exhaustively studied.[56,57] In accordance with these studies, electrodes modified with zeolite NaY incorporating Meisenheimer complex exhibit an oxidation peak in the presence of $NaClO_4$ as electrolyte in DMF. When size-excluded tetrabutylammonium perchlorate was used as electrolyte, the electrochemical response disappeared, since under these conditions only the external surface can be probed due to the impossibility of the bulky electrolyte diffusing inside the pores.



(5)

On the other hand, the electrochemistry of the Meisenheimer complex in LiY, in which larger effects should be observed due to the strength of the interaction, exhibits a reversible redox peak that has never been observed in solution or for the NaY zeolite (Figure 11). We suggest that this reversibility of the Meisenheimer oxidation process is related to stabilisation of the complex and site isolation, which avoid chemical processes coupled with electron transfer.

Chemical reactivity of the Meisenheimer complex encapsulated within zeolites: In agreement with the structure of the Meisenheimer complex and its nature as a reaction intermediate, this carbanion is a highly reactive species that can behave as single-electron donor and hydride donor.[40,58,59] For instance, in anhydrous acetonitrile solution, the Meisenheimer complex readily reacts with molecular O_2 to give probably the superoxide and the corresponding radical, which disproportionates to the Meisenheimer complex and

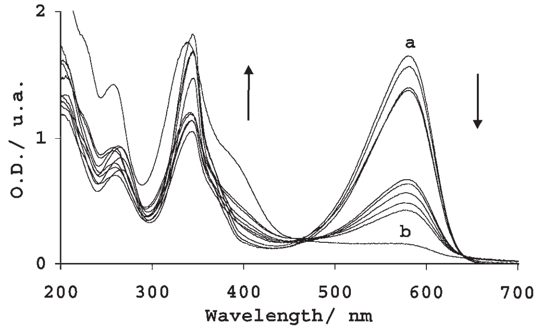
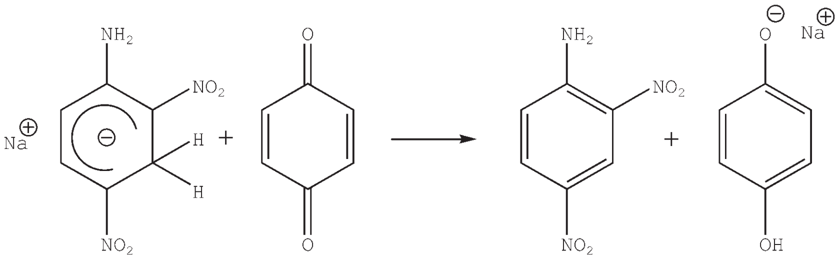


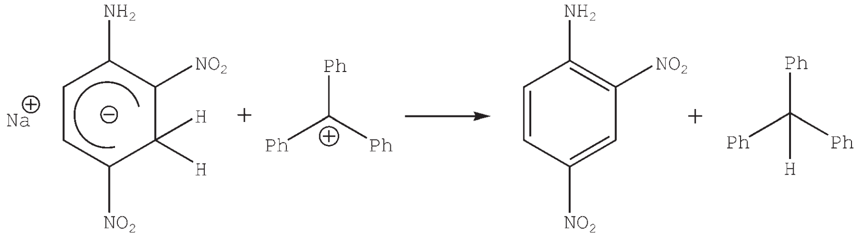
Figure 12. Variation in the optical spectrum of a 10^{-3} M solution of the Meisenheimer complex in aerated DMF with time of exposure to the atmosphere. The time elapsed between the initial (a) and final (b) spectra was 120 min.



(6)

2,4-dinitroaniline as final products [Eq. (5)]. To illustrate this reactivity with O_2, Figure 12 shows the decrease of the characteristic band of the Meisenheimer complex in DMF at 578 nm and the concurrent increase of the 2,4-dinitroaniline band at 350 nm with two isosbestic points at 630 and 465 nm on exposure of the DMF solution to oxygen. At 10^{-3} M in aerated DMF at room temperature, the disappearance of the Meisenheimer complex is almost complete in 120 min. In contrast to this behaviour in solution, when adsorbed in zeolites the Meisenheimer complex can be stored under ambient conditions in the presence of air for more than three months without significant decrease in the intensity of the characteristic Meisenheimer absorption band. However, on stirring a suspension of the zeolite in O_2-saturated, anhydrous acetonitrile for extended periods the formation of some 2,4-dinitroaniline accounting for about 60% of the estimated initial amount can be observed. This indicates that the oxidation process can also take place in the zeolite but at much slower reaction rates and/or for only a certain population of complexes located mostly externally. We suggest that this reduced reactivity is again a manifestation of the stability gained by the Meisenheimer complex when incorporated within the zeolite cages by association with charge-balancing cations. In fact, although no detailed studies have been performed at this stage, the same effect is qualitatively observed in LiCl-saturated DMF solutions, in which the Meisenheimer complex reacts with oxygen about two times slower than in the absence of LiCl.

The higher reactivity towards molecular oxygen of the Meisenheimer complex incorporated in NaY when it is suspended in acetonitrile than as a dry powder can be explained by a combination of factors, including leaching of the Meisenheimer complex into the solution and more favourable oxygen diffusion through the zeolite micropores due to the miscibility of acetonitrile and co-adsorbed water filling the zeolite pores. Both factors make diffusion of O_2 to the target Meisenheimer complex somewhat easier than for dry powders. Dry powders are remarkably more inert towards oxygen than their acetonitrile suspensions and remain unaltered for months.

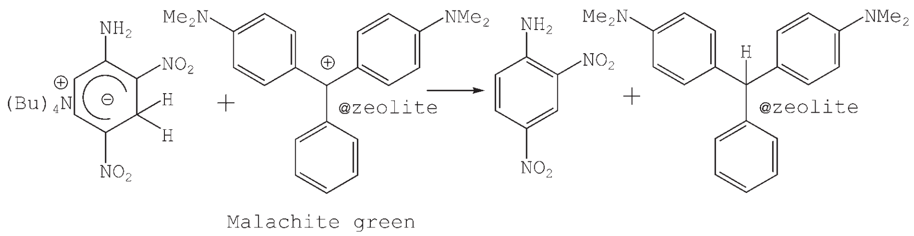


(7)

To learn more about the reactivity of zeolite-incorporated Meisenheimer complexes in electron-transfer processes, we suspended a sample of the zeolite-encapsulated Meisenheimer complex in anhydrous acetonitrile solution containing *p*-benzoquinone. Benzoquinone and Meisenheimer complex instantaneously react[44] by an electron-transfer mechanism [Eq. (6)], followed by electron transfer and proton transfer, to give 2,4-dinitroaniline and hydroquinone anion as final products. Suspensions of zeolite-encapsulated Meisenheimer complex in acetonitrile also react with benzoquinone, and hydroquinone and 2,4-dinitroaniline were detected as reaction products by HPLC after neutralisation. The course of the reaction in different zeolites can be monitored conveniently by UV/Vis spectroscopic monitoring of the increasing concentration of hydroquinone anion over time. In solution this growth is too rapid to be monitored by conventional optical spectroscopy. The above result indicates that the occluded Meisenheimer complex, while remarkably stabilised by entrapment, still exhibit its characteristic reactivity at a much slower rate, most probably after migrating from the solid to the solution.

In the context of the reactivity of the adsorbed Meisenheimer complex, one indirect methodology that has been frequently used to address the internal versus external location of a guest has been to study its reactivity with bulky reagents that cannot diffuse through the entrance of the pores.[60] For this reagent only the guests located at the external surface of the particle are accessible, while those located inside the zeolite particle should be unreactive. We treated the Meisenheimer complex incorporated in three zeolites with triphenylmethyl cation in dry CH_2Cl_2 solution. In homogeneous phase triphenylmethyl cation reacts completely and instantaneously with dissolved Meisenheimer complex to form triphenylmethane and 2,4-dinitroaniline [Eq. (7)]. Triphenylmethyl cation is too large[60,61] to enter the pores and therefore should react exclusively with Meisenheimer complexes located on the external surface of the zeolite particles. As expected from the spectroscopic evidence supporting the location of the Meisenheimer complex within the zeolite pores, triphenylmethyl cation was not able to quench instantaneously all the zeolite-encapsulated Meisenheimer complex but only a fraction. In agreement with Equation (7), the decrease in the population of the Meisenheimer complex was accompanied by the presence of equivalent quantities of triphenylmethane, detected by GC-MS analysis of the solution. Importantly, diffuse-reflectance UV/Vis spectroscopy on the zeolite powders containing the Meisenheimer complex after contact with the solution of triphenylmethyl cation showed that a considerable fraction (ca. 60%) of the initial complexes survived the attack of this powerful, but bulky, hydride acceptor. The fact that triphenylmethyl cation coexists for long periods with the encapsulated Meisenheimer complex in dry CH_2Cl_2 solution, while in the homogeneous phase they react instantaneously, indicates that some Meisenheimer complex must be located within the zeolites pores and protected from prompt hydride abstraction, in agreement with the XPS N/Si atomic profile.[62]

Even more remarkable in terms of lack of reactivity was the fact that zeolite-encapsulated Meisenheimer complex persists for more than three months without decaying in zeolite samples that also contain co-adsorbed water. Water quenches completely the Meisenheimer complex derived from 2,4-dinitroaniline in acetonitrile solution, even in trace quantities. While more understanding of the system is necessary to provide a detailed picture of the reduced reactivity of the Meisenheimer complex with co-adsorbed water and other reagents, we suggest that it is the result of a combination of factors, including: 1) stabilisation of the Meisenheimer complex through strong association with alkali metal ions, 2) immobilisation of co-adsorbed water by strong solvation of the alkali metal ions of the zeolite cages, which renders these water molecules much less reactive than in solution, and 3) confinement of the Meisenheimer complex in a restricted space that imposes geometrical limitations on transition states and on the approach of electrophiles.



(8)

Adsorption mechanism of negatively charged Meisenheimer complex within faujasites: The most reasonable adsorption mechanism of the negatively charged Meisenheimer complex from solution into the internal voids of faujasites with a high density of framework negative charges is that the Meisenheimer complex is adsorbed as an ion pair with the corresponding alkali metal ion. This proposal is consistent with earlier work on "salt occlusion" reported for simple inorganic salts such as NaCl, NaCN and NaI.[17–20,24] We have obtained strong evidence in support of an increase in the ion-pair association constant for occluded Meisenheimer complex. Thus, adsorption of a neutral Meisenheimer/Na^+ ion-pair complex, rather than a negative species, would take place.

To provide some support to this reasonable mechanism, which is compatible with what is known in zeolite chemistry, we prepared the Meisenheimer complex from 2,4-dinitroaniline and tetrabutylammonium borohydride. In the absence of any alkali metal ion, the ion pair consists of the Meisenheimer complex and bulky tetrabutylammonium cation. As mentioned above, studies based on electrochemistry have shown that tetrabutylammonium is size-excluded from the zeolite pores and cannot enter the zeolite micropores.[63] In addition, our UV/Vis spectroscopic measurements indicate that the interaction between the Meisenheimer complex and tetrabutylammonium cation is very weak, since high tetrabutylammonium concentrations in DMF (1 M) do not produce any significant shift in Meisenheimer λ_{max}, as opposed to what was observed for Na^+ and Li^+ ions. In contrast to a solution of the Na^+ salt, which is immediately adsorbed inside NaY, the tetrabutylammonium salt of the Meisenheimer complex under identical conditions is adsorbed only in part, and a significant concentration of the Meisenheimer complex remains in solution even for prolonged times, as evidenced by the optical spectrum of the supernatant solution. Moreover, the characteristic color of the Meisenheimer complex fades immediately on filtering the solid and exposing it to the atmosphere, a similar behaviour as when adsorbed on silicas. This suggests exclusive external location of the minor fraction of the Meisenheimer complex adsorbed when tetrabutylammonium is the accompanying cation.

To follow the diffusion of Meisenheimer complex through the interior of the zeolite particle and not just mere adsorption on the external surface, adsorption of the Meisenheimer/tetrabutylammonium ion pair was studied with a zeolite containing malachite green, which should react according to [Eq. (8)]. Malachite green is a dye with triarylmethyl cation structure that can be readily prepared inside the cavities of zeolite Y by ship-in-a-bottle synthesis from benzaldehyde and *N*,*N*-dimethylaniline.[62] After synthesis, malachite green remains immobilised inside the zeolite supercages without any possibility of diffusion through the micropores due to its large molecular size. As expected, contacting zeolite containing malachite green with a fivefold excess of the tetrabutylammonium salt of the Meisenheimer complex in DMF does not lead to complete disappearance of the malachite green, but a substantial fraction of the zeolite-encapsulated malachite green remains in the presence of the Meisenheimer/tetrabutylammonium ion pair for long periods (6 h). In DMF solution, the Meisenheimer complex and malachite green react instantaneously through a formal hydride-transfer mechanism. This incomplete reaction of adsorbed malachite green and Meisenheimer complex indicates that the Meisenheimer complex exhibits impeded diffusion with tetrabutylammonium as counterion.

All the above comparative adsorption experiments are consistent with a strong influence of the countercation on diffusion, in agreement with our proposal of adsorption of Meisenheimer complex as an ion pair.

Conclusion

We have provided evidence in support of the incorporation of a highly reactive carbanion intermediate inside zeolites. Although there are precedents for adsorption of simple inorganic anions in zeolites, adsorption of an elusive organic anion is unprecedented. The internal location of the Meisenheimer complex was inferred by comparison with the behaviour observed for amorphous SiO_2 and SiO_2–Al_2O_3 (25 wt %) and from the atomic profile of C and N versus the depth of penetration provided by XPS analysis. Since the electroneutrality principle must be maintained and the ingress of the Meisenheimer complex must be accompanied concurrently by the ingress of a countercation, evidence has been presented that the actual species being adsorbed is a neutral cation/Meisenheimer ion pair by an adsorption mechanism of the salt-occlusion type. Therefore, the nature of the accompanying cation has a strong influence on the adsorption. For Li^+ and Na^+ ions, this ion pair seems to form a strong complex within the zeolite cavities that exhibits a spectral blue shift in λ_{max} of more than 100 nm. An unforeseen remarkable stabilisation of incorporated Meisenheimer complex has been observed. This stabilisation is responsible for sluggish reactivity of the zeolite-entrapped reaction intermediate. This effect probably arises from a dramatic enhancement of the association constant of this negatively charged intermediate with the Na^+ and Li^+ ions and from the spatial confinement within the zeolite pores. We are now exploring the generality of this adsorption mechanism and the possibility to adsorb and stabilise other organic carbanions.

Experimental Section

Materials and methods: NaX and NaY were commercial zeolites (P.Q. Industries). LiY was obtained from NaY by Na^+/Li^+ ion exchange with a 0.4 M aqueous solution of LiCl at 60 °C and a solid/liquid ratio of 1/10 for 2 h with magnetic stirring. The solid was collected by filtration, washed with copious distilled water and submitted to a second ion-exchange step under the same conditions as before but with 0.6 M LiCl. HBeta was obtained by hydrothermal crystallisation with tetrapropylammonium hydroxide as structure-directing agent followed by calcination in air[64] (Si)Beta was obtained by hydrothermal crystallisation with tetrapropylammonium ion as structure-directing agent and Aerosil silicon sources. NaBeta was obtained from HBeta by H^+/Na^+ exchange with 0.4 M aqueous Na_2CO_3 solution and a solid/liquid weight ratio of 0.1 at 60 °C for 2 h. The resulting partially exchanged NaBeta was submitted to a second ion-exchange step as before but with 0.6 M Na_2CO_3 solution. SiO_2 and SiO_2–Al_2O_3 (25 wt %) were commercial samples (BASF). SiO_2 and SiO_2–Al_2O_3 were subjected to ion exchange with an aqueous 0.4 M solution of Na_2CO_3 at a solid/liquid ratio of 1/10 for 2 h at room temperature to neutralise any possible surface acid sites. Dehydroxylated SiO_2 was obtained by heating commercial BASF SiO_2 to 900 °C for 5 h.

Optical spectra were recorded with a Cary 5G UV-VIS-NIR spectrophotometer in transmission or diffuse-reflectance aquisition mode. For transmission quartz cuvettes (1 cm × 1 cm) capped with septa were used. For diffuse reflectance a praying mantis accessory was adapted to the instrument and $BaSO_4$ was used as reference. The diffuse-reflectance data were plotted as the Kubelka–Munk function $F(R)$.[65]

Square-wave voltammograms were recorded with a BAS CV50W equipment. Semiderivative treatment of data was used to improve peak resolution. A standard three-electrode arrangement was used with a platinum auxiliary electrode and a AgCl (3 M NaCl)/Ag reference electrode, separated from the bulk solution by a salt bridge, in a cell thermostated at 298 K. MeCN solutions of $LiClO_4$ (Aldrich), Et_4NClO_4 (Acros) and Bu_4NPF_6 (Fluka) in 0.10 M concentration were used as supporting electrolytes. Experiments with forced convection were performed by vigorously bubbling argon through the cell by means of a capillary located close to the working electrode. Sample-modified polymer-film electrodes were prepared by transferring a few microlitres (typically 50 μL) of a dispersion of the solid (10 mg) in acetone (5 mL) to the surface of a freshly polished glassy carbon electrode (GCE, geometrical area 0.071 cm^2) and allowing the coating to dry in air. Then one drop of a solution of acrylic Paraloid B72 resin (1 %) in acetone was added and the modified electrode was air-dried. The coatings examined contained 0.2–1.5 $mg\,cm^{-2}$ of dry sample.

XPS measurements were carried out at room temperature with a concentric hemispherical analyzer operated in the constant-pass energy mode (50 eV). An $Mg_{K\alpha}$ X-ray source ($h\nu = 1253.6$ eV) was used. A vacuum of about 5×10^{-9} Torr was always maintained in the analysis chamber during XPS recording. Charging effects were calibrated by the C (1 s) line at 284.6 eV.

Preparation of hydride Meisenheimer complex of 2,4-dinitroaniline: The sodium or tetrabutylammonium salts of the Meisenheimer complex of 2,4-dinitroaniline (Aldrich, recrystallised from ethanol before use) was prepared by adding a solution of sodium or tetrabutylammonium borohydride (1.7 mmol) in anhydrous acetonitrile (20 mL) to a stirred solution of 2,4-dinitroaniline (2.3 mmol) in the same solvent (10 mL). The reaction vessel was continuously flushed with dry argon and protected from light. The mixture was stirred for 90 min and then slowly added to an excess of cold anhydrous diethyl ether. The required salt precipitated from the solution on standing at 0 °C. The Meisenheimer complex was purified by redissolving the solid in anhydrous acetonitrile and reprecipitating with cold anhydrous diethyl ether under a flow of dry argon. The salts of the hydride Meisenheimer complex are dark violet solids and were characterised by ^1H NMR, ^{13}C NMR and UV/Vis spectroscopy; the spectra were coincident with those reported in the literature.[44]

Adsorption of Meisenheimer complex in X and Y faujasites and on other solids: The adsorption of Meisenheimer complex in X and Y faujasites or on other solids was carried out by stirring for 90 min under inert atmosphere a solution of Meisenheimer complex (15 mg, 0.071 mmol) in anhydrous acetonitrile (10 mL) in the presence of the faujasite or other solid (500 mg) that was previously thermally actived (500 °C, overnight). After this time, the suspension was filtered, and the solid was submitted to continuous solid–liquid extraction in micro-Soxhlet equipment with acetonitrile as solvent under argon atmosphere.

Malachite green encapsulated within zeolite Y was prepared as previously reported by reaction of benzaldehyde (100 mg) with *N*,*N*-dimethylaniline (2 mL) in the presence of thermally dehydrated HY zeolite at reflux temperature for 5 h.[62] The resulting green solid was collected and submitted to a series of consecutive continuous solid–liquid extractions with toluene, dichloromethane and acetone. The solids were exhaustively evacuated to remove solvents before being used in the adsorption studies.

Acknowledgements

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