Intrazeolite Photochemistry. 8. Influence of the Zeolite Physicochemical Parameters on the Laser Flash Photolysis of 1,1-Diphenyl-2-Propanone Included in Acid Faujasites

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Abstract: Time-resolved diffuse reflectance laser flash photolysis studies of 1,1-diphenyl-2-propanone (DPA) included in a consistent series of Y faujasites at four levels of Na^+-to-H^+ exchange have shown that the interaction of this guest molecule with the zeolite acid sites leads to transient spectra much different than that due to the diphenylmethyl radical ($DPM^\cdot$) characteristic of nonacidic hosts. Similar modification of the photochemical pattern was also observed when DPA was adsorbed onto the all-Lewis acid site ZnY zeolite, albeit much slower decay traces were recorded in this case. We have found that by using a highly dealuminated acid zeolite (HYD, Si/Al 27.5) a much better resolved transient spectrum characteristic of the diphenylmethyl cation (DPM^+) was obtained. Methanol quenching experiments have provided firm evidence for the generation of DPM^+ within acid zeolites. A progressive increase of the $DPM^\cdot/DPM^+$ ratio, as measured from the relative intensities of their corresponding signals, with the time elapsed from the preparation of the complexes has been observed. Finally, the effects of coadsorbed water and the presence of oxygen on the spectra and the kinetics of the transients generated from DPA are reported.

Introduction

Photolysis of dibenzyl ketone and other related phenyl-substituted acetones adsorbed within medium- and large-pore zeolites has been extensively employed as a means to generate benzyl radicals that report on the topological structures they experience.[1] In this type of study, where the zeolite framework provides the walls that define a confined space, little attention has been focused on the role that the charge-compensating cations located within the solid micropores play on the course of the photochemical reaction.

Zeolites are crystalline aluminosilicates where the presence of each AlO_4 tetrahedron creates an excess of framework negative charge that must be compensated by the presence of charge-balancing cations.[2] The ionic nature of the chemical bond between these cations and the zeolite framework makes them susceptible to exchange without producing any alteration of the solid lattice. The influence of alkaline cation exchange on the reactions of benzyl radicals formed by photolysis of dibenzyl ketones has been occasionally pointed out but was described as being due to the modification of the "lebensraum" available to the radicals during their migration through the global and local internal spaces.[3] Therefore, changes in the product distribution for the distinct environments arise from the different location and timing of radical recombination, while the primary photochemical processes of the dibenzyl ketones such as intersystem crossing and homolytic bond breaking are still common and independent of the environment for homogeneous solution and intrazeolite irradiations. Similar effects caused by the modification of the free volume available to the organic guest molecules depending on the number and size of the alkaline cations present in the faujasite supercages have been observed in the photolysis of alkyl deoxy benzoins[4] and aryl alkyl ketones.[5] On the basis of product studies, it has been proposed that Lewis acid interactions between the charge-balancing cation and the guest organic molecules can alter the ratio between Norrish type I and type II processes undergone by aryl alkyl ketones.[6] Recently, a cooperative effect of acid sites on the photocyclization of azobenzene adsorbed on large-pore zeolites has been established.[7]

In the present work, we have employed time-resolved diffuse reflectance techniques[8] to show that the interaction of Brönsted and Lewis acid charge-compensating cations of the zeolite with 1,1-diphenyl-2-propanone (DPA) and 1,1,3,3-tetraphenyl-2-propanone (TPA) can divert their "normal" photochemical behavior characterized by the formation of diphenylmethyl radicals ($DPM^\cdot$)[9] Moreover, a relationship between the physicochemical parameters of the zeolite and the extent of modification of the photochemical pattern of the hosted molecules has been observed, thus allowing a characterization of the acid strength and nature of the acid sites involved.

Experimental Section

Materials. DPA (1,1-diphenyl-2-propanone) was a commercial sample (Aldrich) and used as received. TPA (1,1,3,3-tetraphenyl-2-propanone) was synthesized by condensation of ethyl diphenylacetate using sodium metal, following the reported procedure,[10] and purified by flash column chromatography using hexane as eluent.

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NaY was a commercial sample (Aldrich, LZY52 molecular sieves). The partially or totally exchanged HY21, HY50, and HY100 zeolites, where the number indicates the percentage of Na^+ removed and determined by chemical analyses, were prepared by treating NaY at room temperature with aqueous solutions of NH_4AcO followed by drying at 383 K for 6 h and deep-bed calcination at 823 K as previously reported.[11]

The dealuminated HYD sample was obtained by treating NaY with $SiCl_4$ at 723 K for 3 h, following the method described in the literature.[12] The resulting solid was subjected to two consecutive exchange–calcination cycles using 0.40 and 0.60 M aqueous solutions of NH_4AcO. The final Na^+ content expressed as Na_2O was 0.03 wt %, while the crystallinity was 95% of the original NaY. The unit cell size measured by X-ray diffraction was 24.24 Å.

ZnY was prepared by initially treating the NaY zeolite with a 0.5 M aqueous solution of $Zn(NO_3)_2$ followed by drying and calcination using the same conditions as above. The resulting solid was treated with a NaCl solution and then subjected to a final exchange–calcination process using a 1 M aqueous solution of $Zn(NO_3)_2$. The solid-to-liquid ratio used in all the exchange steps was 1:10. Chemical analysis of the solid showed that the Zn content was 1.87 mmol g^{-1}.

Characterization of the nature and the acid-strength distribution of the acid sites was performed by IR (Perkin-Elmer 580 B spectrophotometer equipped with a data station) using wafers of 10 mg cm^{-2} pretreated at 473 K and 10^{-3}-Pa dynamic vacuum for 2 h following the pyridine adsorption–desorption protocol.[13]

Preparation of the Zeolite-Organic Material Complexes. A solution of the organic ketone (about 25 mg) in dichloromethane (30 mL) was poured onto the appropriate zeolite (1.00 g) activated by baking at 773 K for 20 h prior to use. The resulting suspension was magnetically stirred for 2 h and then centrifuged, washed with fresh dichloromethane (5 mL) for 30 min, and again centrifuged. The amount of organic material adsorbed was calculated from the difference between the initial amount and that recovered in the combined dichloromethane solutions measured by UV absorption. The samples were dried under vacuum to ensure complete solvent removal and stored and handled without any special precautions.

The stability of the organic ketones after adsorption on acidic zeolites was tested by preparing a sample of DPA (29.1 mg) on HY100 (1.00 g) as above. After the complex was left for 7 days at room temperature in the open air, the solid was subjected to continuous solid–liquid extraction using dichloromethane as solvent. The recovered amount accounted for 89% of the material included, while GC analysis showed that 92% of the mixture was DPA.

Laser Flash Photolysis. The experimental setup for diffuse reflectance is similar to that described in detail previously.[14] The fourth harmonic (266 nm; ≤10-ns pulses; ≤10 mJ/pulse) from a Surelite Nd:YAG laser was used for sample excitation except for the dose experiments, for which a Lumonics EX-510 excimer laser (Xe/HCl/He, 308 nm) was used, along with a set of neutral density filters to attenuate the energy per pulse. The data analysis was based on the fraction of reflected light absorbed by the transient: reflectance change = $\Delta J/J_0$, where J_0 is the reflectance before excitation and ΔJ is the change in the reflectance after excitation. For low values of reflectance change this function is linear with concentration.

Samples contained in 3 × 7-mm^2 quartz cuvettes were either purged with nitrogen for 30 min or outgassed by heating at 351 K under dynamic vacuum for 1 h and sealed prior to use. Selective evacuation of water from the aged complexes was attempted by heating at 327 K under dynamic vacuum for 1, 2, and 8 h. Methanol quenching experiments were carried out by connecting under vacuum the outgassed DPA–HYD complex and a thermostated flask containing methanol (BDH, Omnisolv) previously subjected to four freeze–pump–thaw cycles. In all cases, photolysis was carried out at room temperature.

Results and Discussion

Inclusion of DPA or TPA onto the solid hosts was carried out by allowing free diffusion of the organic material between a dichloromethane solution and the thermally activated solid. Although the exact amount of material adsorbed varied in each sample, the average value was about 1 wt %, which corresponds approximately to a level of occupancy of 10% of the faujasite supercages.

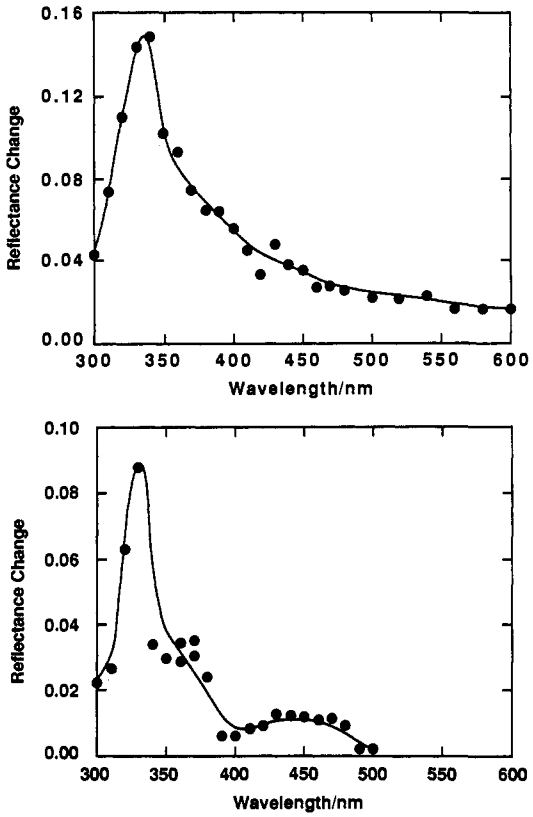

Figure 1. Transient spectra recorded 3.2 μs after 266-nm excitation of the DPA–NaY composite (top) without treatment and (bottom) after outgassing at 351 K under 10^{-1} Torr for 1 h.

The photolysis of DPA was initially carried out adsorbed onto a nonacidic NaY zeolite (DPA–NaY composite) using 266-nm excitation. The transient spectrum obtained 3.2 μs after laser excitation is presented in Figure 1(top). This spectrum matches that reported for DPM$^\bullet$ adsorbed on NaX zeolite, generated by laser flash photolysis of TPA,[15] and is reasonably close, albeit broader, to that reported for DPM$^\bullet$ in solution.[16]

$$Ph_2CHCOCH_3 \xrightarrow{h\nu} Ph_2CH^\bullet + {}^\bullet COCH_3 \qquad (1)$$

This result is in agreement with the well-known photochemical behavior of DPA as a source of DPM$^\bullet$, eq 1, and also with the fact that NaX and NaY faujasites have identical topological geometries, differing only in the framework Si/Al ratio and hence in the number of Na^+ ions per unit cell.

In order to learn about the influence of chemisorbed air and water present within the zeolite micropores on the course of the photolysis, the spectrum of the DPA–NaY sample was also recorded after heating at 351 K under vacuum for 1 h, Figure 1 (bottom). This treatment did not change the position of the maximum at ~330 nm but led to a narrower band with only very weak reflectance at wavelengths longer than 400 nm. In addition, a remarkable enhancement of the DPM$^\bullet$ decay rate was observed in the activated sample as illustrated in Figure 2. The change in kinetics can be rationalized assuming that spectator molecules adsorbed from the environment are impeding the free mobility

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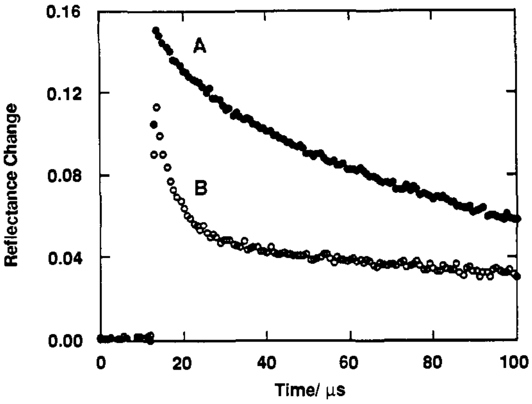

Figure 2. Transient decay traces monitored at 330 nm after 266-nm excitation of DPA–NaY (A) without treatment and (B) after pumping at 351 K under 10^{-1} Torr for 1 h.

of DPM$^{\bullet}$ inside the voids, thus making the migration of the radicals inside the isotropic solid more difficult and increasing their lifetime. DPM$^{\bullet}$ is expected to react largely with its original radical partner,[17] as these processes are far more probable than random recombinations. This result is not surprising upon consideration that the water content of these hydrophilic zeolites can be as high as 20 wt % and that we are dealing with samples in which the DPA content (by weight) can be 1 order of magnitude lower than the amount of water. In addition, changes in the water content may influence the location and/or the mobility of DPA. Similar restrictions in the mobility of benzyl radicals due to the presence of coadsorbed spectator molecules are thought to cause variations in the cage effect.[18]

Influence of the Strength and Nature of Acid Sites on Photolysis. Laser flash photolysis experiments were also carried out with DPA included onto a systematic series of acidic HY zeolites (HY21, HY50, and HY100, where the number indicates the level of Na^+ exchanged) prepared by NH_4^+-to-Na^+ exchange followed by thermal deamination at 823 K. In contrast to the DPA–NaY composite, the transient spectra recorded for these three zeolites showed a structureless broad reflectance change in the 300–550-nm region. The spectra obtained from the DPA–HY50 and DPA–HY100 complexes are illustrated in Figure 3. Interestingly, the transient decay profiles changed at different wavelengths, with those in the 330-nm region being significantly faster than those recorded near 440 nm, Figure 4. This difference in the rates indicates that more than one species is decaying within the time domain monitored. These results clearly show that the acid sites of the HY zeolites are intervening in the course of the photolysis and imply that at least one other intermediate besides DPM$^{\bullet}$ needs to be invoked when DPA is included in acidic zeolites.

On the other hand, it is well known that the percentage of NH_4^+-to-Na^+ exchange not only determines the total number of acid sites present in the zeolite, one center per NH_4^+ exchanged, but also, in the case of faujasites with a low framework Si/Al ratio, results in remarkable changes in the acid-strength distribution of the sites.[19] It has been established that the population of strong acid sites, those with $pK_a < 0$, increases exponentially with the level of ion exchange, i.e., only the HY100 sample has an appreciable number of this type of sites. Therefore, the fact that modification of the transient spectrum occurs even upon inclusion on weakly acidic HY21 and HY50 samples constitutes a strong indication that all the acid sites, regardless of their acid strength, are able to alter the photochemistry of DPA in a similar manner. In this context, it has been recently suggested that protonation of the excited states of aromatic ketones can occur even on nonacidic Na^+-containing zeolites.[20]

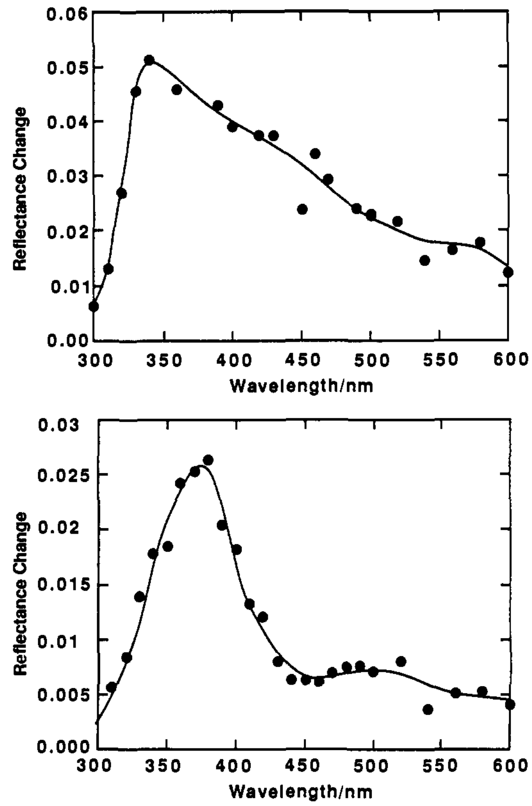

Figure 3. Transient spectra recorded 3.6 μs after 266-nm excitation of (top) DPA–HY50 and (bottom) DPA–HY100.

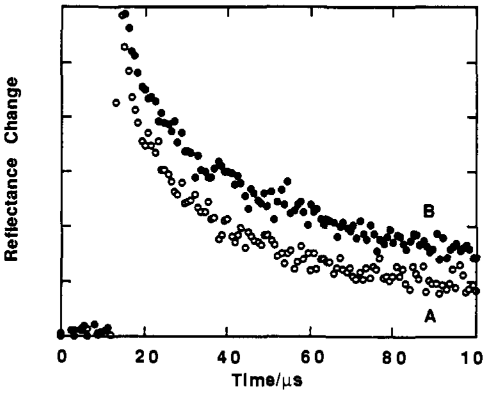

Figure 4. Transient decay traces after 266-nm excitation of DPA–HY50 monitored at (A) 330 nm and (B) 440 nm. The traces have been normalized.

We were interested in establishing if any interaction between the zeolite active sites and the substrate takes place in the ground state or if it occurs exclusively in the excited states. To address this question, both the reflectance and fluorescence spectra of DPA included onto NaY and HY100 were recorded, Figure 5. As a matter of fact, the reflectance spectrum of DPA adsorbed on NaY, Figure 5A, and the absorption spectrum in dichloromethane solution exhibit the same characteristic features, indicating that DPA does not experience a strong interaction when adsorbed on NaY. Notably, in the case of the totally exchanged HY100, the low extinction coefficient band centered above 300 nm and assignable to the $n \rightarrow \pi^*$ absorption of the ketone chromophore is absent, Figure 5B. This can be explained by assuming that the oxygen lone electron pair of the ketone group required for this absorption to occur is blocked by strong

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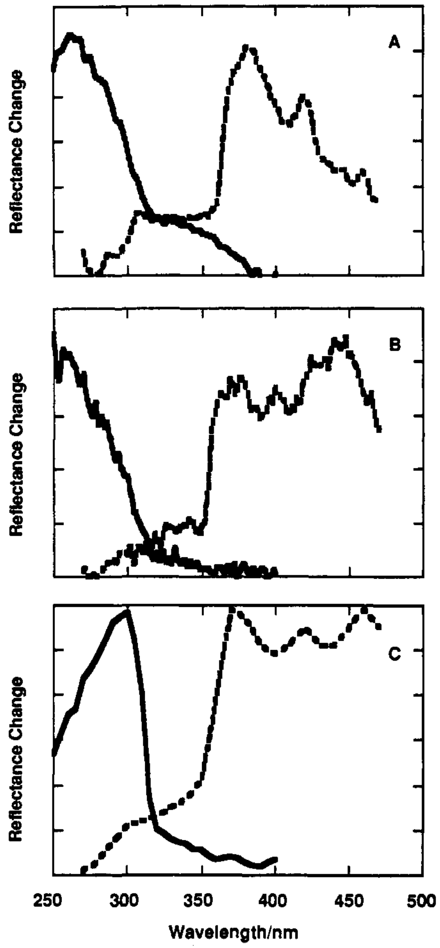

Figure 5. Diffuse reflectance (solid line) and emission (dashed line) spectra using 250-nm excitation of (A) DPA–NaY, (B) DPA–HY100, and (C) DPA–HYD. The spectra have been normalized, and arbitrary units and shifts have been used for the vertical scales.

interaction with the acid sites present in the zeolite surface. Taking into account that the loading level of DPA has been kept low with an average of 1 molecule every 10 α–cages and that each α-cage has a large population of accessible acid sites (40 potential sites), our explanation is in good agreement with the widespread use of these types of acid zeolites as catalysts for thermal ground-state reactions involving ketone-group protonation.[21] The fluorescence spectra of DPA–NaY and DPA–HY100 show considerable differences at wavelengths greater then 400 nm, Figure 5, reflecting again the different environments experienced by the guest molecules.

Given that in the ground state most carbonyl group reactions can be catalyzed both by Brönsted and Lewis acids, we tried to assess if the modification of the transient spectra in the way observed for the HY samples could also be accomplished using Lewis acid zeolites. With this objective in mind, we prepared a ZnY sample from NaY by two consecutive ion-exchange treatments using increasing concentrations of aqueous $Zn(NO_3)_2$ solutions, separated by an intermediate neutralization step to avoid Brönsted sites generated by water hydrolysis of solvated Zn^{++} ions during the calcination steps,[22] eq 2. With this pretreatment, the samples could be activated without complications.

$$Zn(H_2O)^{++} \rightarrow Zn(OH)^{+} + H^{+} \qquad (2)$$

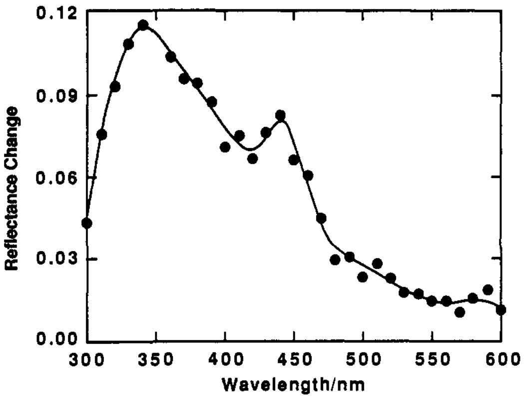

Figure 6. Transient spectrum of DPA–ZnY recorded 4.6 μs after 266-nm excitation.

Chemical analysis of the ZnY sample showed that essentially total exchange of Na^+ for Zn^{++} had taken place. The Brönsted or Lewis nature of the acid sites of the resulting ZnY zeolite was characterized by the pyridine adsorption–desorption method. Pyridine when adsorbed on acid solids gives rise in the IR spectrum to specific bands associated with the pyridinium ion (1550 cm^{-1}) and with Lewis-acid-coordinated pyridine (1450 cm^{-1}). The relative intensity of the two bands can be used for a quantitative determination of the population of both types of centers. The pyridine spectrum after adsorption onto ZnY and evacuation at 473 K for 1 h showed that in contrast to the HY series, ZnY contains only Lewis sites and is essentially free of Brönsted sites, in good agreement with previously reported data.[23]

When laser flash photolysis was carried out on DPA adsorbed onto ZnY (DPA–ZnY composite), the transient spectrum recorded showed two defined maxima, one centered at 330 nm assignable to DPM· and the other around 440 nm, Figure 6. The decay profiles of the two maxima are significantly slower than those for the previous composites, probably indicating that the mobility of the transient species is severely reduced by the presence of Zn^{++}, a cation of comparable crystalline ionic radius to Na^+ but much more acidic.

As already noted, in contrast to the case of the NaY faujasite, the transient spectra recorded for DPA included in the HY series consisted of unresolved broad bands. The observed differences can be reasonably ascribed to the presence of DPA in different environments. Moreover, this inhomogeneity arises mainly from the presence on the zeolite surface of a large variety of acid sites differing in their chemical environment. In order to test if a more uniform distribution of the strength of the acid sites could lead to a better defined spectrum that would allow a deeper insight on the nature of the transients involved, we prepared a highly dealuminated HYD zeolite.

It has been established that the strength of a particular acid site depends on the number of Al atoms present in the next nearest neighborhood (NNN), with acid strength increasing as the number of Al NNN decreases.[24] Therefore, the framework Si-to-Al ratio is one of the most important physicochemical parameters to be considered in order to control the acid-strength distribution of the sites. Dealuminating causes not only a decrease in the total number of acid sites, one per each framework Al removed, but also an increase in the average strength of the remaining sites, up to a framework Si-to-Al ratio in which all the sites will have mainly zero Al NNN and therefore essentially the same acidity. At that point, further dealumination does not cause any additional change in the acid distribution but merely decreases the number of sites.

Preparation of the dealuminated NaYD zeolite was accomplished by treatment of NaY (Si/Al 2.4) with $SiCl_4$ at 773 K,

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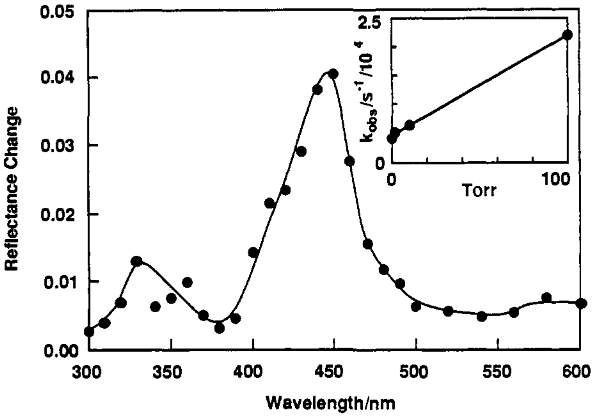

Figure 7. Transient spectrum recorded 3.6 μs after 266-nm excitation of the (freshly prepared) DPA–HYD composite. Inset: plot of the apparent rate constants obtained from the 5-μs time scale against the methanol vapor pressure for DPA–HYD.

following reported procedures.[12] The unit cell size measured by X-ray diffraction was 24.24 Å, while the resulting framework Si/Al molar ratio was 27.5, which corresponds to an average of less than one Al per α-cage. Finally, this dealuminated NaYD was subjected to NH_4^+-to-Na^+ ion exchange under the same conditions as those used for HY100. Chemical analysis established that total ion exchange had occurred. It has been found that acid faujasites with a framework Si/Al ratio higher than 15 possess mainly sites with zero and a small percentage of one Al NNN. Therefore, we conclude that our HYD zeolite is a homogeneous solid from the point of view of the acid-strength distribution of its sites. This special characteristic of the HYD sample is reflected in the ground-state reflectance spectrum of the guest DPA, Figure 5C, where besides the absence of the $n \rightarrow \pi^*$ band due to the C=O chromophore, as with the DPA–HY100 complex, a remarkable shift of the aromatic reflectance is observed. The fluorescence spectrum of DPA–HYD after 250-nm excitation, Figure 5C, is also much more similar to that of DPA–HY100 than to the spectrum generated with the nonacidic NaY.

The transient spectrum of the resulting DPA–HYD composite recorded 3.6 μs after laser excitation is shown in Figure 7. This spectrum exhibits one large band centered at 440 nm and a weaker band at 330 nm; the two bands showed distinctive decays and are attributed to the DPM carbocation (*vide infra*) and radical, respectively. A comparison of the results attained for the series at different levels of NH_4^+-to-Na^+ exchange and a low framework Si-to-Al ratio, Figure 3, with those achieved for the highly dealuminated HYD zeolite, Figure 7, constitutes experimental evidence that sites of different acid strength and framework chemical environment induce different interactions, the broadness of the spectra for HY21, HY50, and HY100 being the consequence of the inhomogeneity of the centers. In other words, transient species generated in the neighborhood of different sites would not exhibit exactly the same spectroscopic characteristics or relative abundancies.

When the spectra of Figures 3 and 6 are compared with those of Figures 1 and 7, it seems likely that another species with reflectance in the 380–400-nm region may be involved in the system in addition to the radical, Figure 1, and the carbocation, Figure 7. While overlapping signals make any conclusion on this additional intermediate speculative, it is possible that highly conjugated products resulting from radical coupling at the ortho and para positions may be involved. Such products would be expected to show transient behavior and to rearomatize readily in the acid environment provided by the zeolites. The spectra of the radical and carbocation are nonetheless unequivocal, and conclusions regarding these species should not be affected by the presence (only under some conditions) of an additional species in the 380–400-nm region.

Another interesting effect worth mentioning is that in the case of the DPA–HYD composite, no differences were found in the transient decays with and without prior evacuation of spectator molecules by heating the sample at 351 K under vacuum for 1 h. Since it is well known that the hydrophilicity of a zeolite is related to its framework Si-to-Al ratio,[25] with highly dealuminated zeolites being more hydrophobic, the observation that the decay traces obtained using dealuminated samples are unaffected by evacuation while the decay traces using low Si-to-Al ratio samples (i.e., DPA–NaY composite) are strongly affected can be simply due to differences in the water chemisorption properties between these samples. In particular, differences in the water content of HY100 and $SiCl_4$-dealuminated acid Y zeolite have been reported.[26] Moreover, the relationship between the framework Si/Al ratio and the modification of the decay by prior evacuation indicates that mainly water, and not oxygen, is the species responsible for these changes.

Effect of Composite Aging. The results discussed so far were found to be reproducible by performing an independent preparation of several batches of the complexes. In contrast, we have observed differences in the behavior of the transients in each sample depending on the time elapsed between the inclusion of DPA and the photolysis. The decay at 330 nm for the DPA–HY100 composite immediately after its preparation was much faster than that recorded after several days; however, no appreciable differences were found between the 5th and 15th day under our laboratory conditions.

In spite of the changes in the kinetics, the transient spectra remained unchanged for the first 15 days after sample preparation, although longer periods of aging resulted in the observation of significantly altered spectra. As illustrated in Figure 8, the aging of the samples for 90–120 days always leads to an increase of the relative ratio of the 330-nm signal to the 440-nm signal. In particular, a comparison of Figure 8D with Figure 7 is quite revealing. Eventually, a spectrum closely resembling that of NaY was recorded even for the highly acidic HY100 zeolite. The change in transient spectra as a function of aging was not due to decomposition of DPA which was completely recovered by exhaustive solid–liquid extraction from an aged DPA–HY100 sample.

Heating an aged sample under dynamic vacuum for 1 h at 351 K had no effect on the shape of the spectra. It did, however, lead to a progressive decrease in the intensity of the reflectance signal, such that the signals disappeared completely when the samples were treated at 427 K for 8 h.

We believe that all these observations can be easily rationalized in terms of the variable amount and the location of evacuated water after the activation procedure and while an equilibrium state is being reached. Thus, initial lower water content for the highly hydrophilic HY100 zeolite should lead to faster DPM· decays, as we already noticed for the outgassed DPA–NaY composite.

The changes in the transient spectra of aged samples reveal that diffuse reflectance signals at wavelengths longer than 400 nm are specifically associated with the interaction of DPA with the zeolite acid sites. Therefore, if the more basic water molecules compete by displacing DPA from these centers, one should expect a spectrum comparable to that obtained for DPA–NaY, where there is essentially no interaction. Once water has replaced DPA, only selective water desorption (which appears not to be the case) could revert the situation.

In order to avoid the problems originating from the aging of the composites and to ensure reproducible data, all the samples

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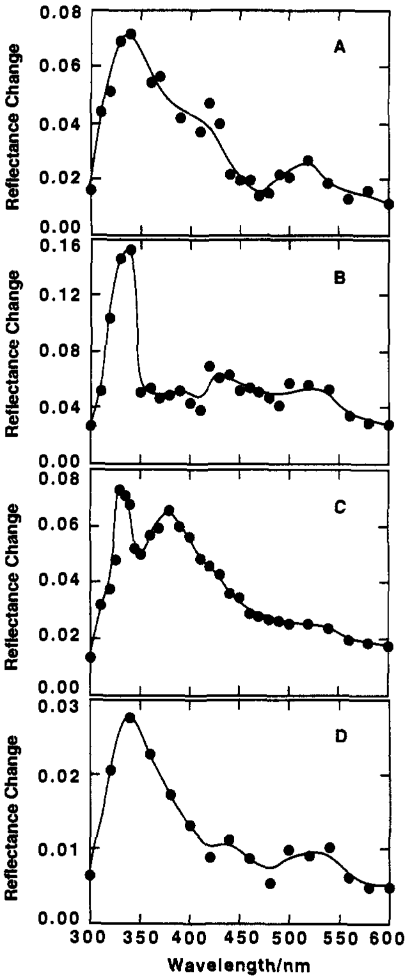

Figure 8. Effect of the aging of the composites on the transient spectra obtained under the same conditions as indicated in Figures 3, 6, and 7, respectively: (A) DPA–HY100 90 days after preparation, (B) DPA–HY100 120 days after preparation, (C) DPA–ZnY 120 days after preparation, and (D) DPA–HYD 120 days after preparation.

were stored under laboratory conditions without any special precautions. Photolysis was then performed within 7 days, following the preparation of the composite, while the spectra showed the characteristic features of the guest–host interaction.

Quenching Experiments. The results obtained for DPA included on HYD indicate that there are two different transients decaying in the time domain monitored. The transient responsible for the reflectance change in the 330–350-nm region in the DPA–HYD complex can be reasonably assigned as DPM$^{\cdot}$. Its maximum has been reported at 340 nm in NaX faujasite,[17] while we have observed it at 330 nm in the NaY sample, Figure 1. The spectral shift in DPA–HYD is not uncommon, particularly if the differences in hydrophobicity and charge density of the solid surfaces are considered. The second transient absorbing at 440 nm can be confidently assigned to the DPM carbocation (DPM$^+$) on the basis of the fact that its spectrum is in full agreement with that observed for DPM$^+$ in solution.[16] Furthermore, the transient is formed preferentially in the acid zeolites and is reactive toward methanol, *vide infra*, as expected for DPM$^+$. In addition, the chemical ionization–mass spectra of DPA and TPA, which show the gas-phase behavior of the corresponding protonated molecules, give DPM$^+$ as the most intense peak.

In order to gain some support for our proposals, quenching experiments were undertaken. However, quenching and scavenging in zeolite media are not as straightforward as in liquid solutions. We initially investigated the influence of oxygen on the decay of DPM$^{\cdot}$ generated in the DPA–NaY composite with and without prior evacuation of the water adsorbed onto the zeolite.

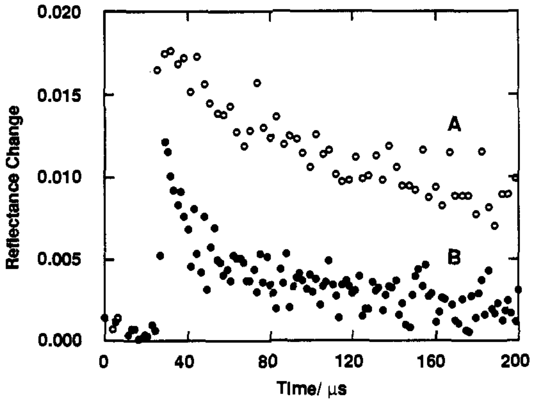

Figure 9. Transient decay traces monitored at 440 nm (A) before and (B) after methanol quenching (298 K) of evacuated DPA–HYD using 266-nm excitation.

Surprisingly, no difference in the intensity or the rate of decay of the 330-nm signal was found for DPA–NaY samples purged with nitrogen or under an oxygen atmosphere. By contrast, if this composite was submitted to evacuation prior to the photolysis experiments, the presence of oxygen led to a significant decrease in signal intensity, while the rate of decay of the remaining radicals was remarkably coincident with that recorded without the outgassing treatment.

These results show that oxygen diffusion through the faujasite micropores as well as the quenching process are strongly impeded by the presence of water filling the zeolite voids. The fact that the presence of oxygen in the evacuated sample led to a decrease in the reflectance signal constitutes an indication that a fraction of DPM$^{\cdot}$ is quenched by oxygen in a time domain shorter than that we are monitoring. On the other hand, the long-lived population of DPM$^{\cdot}$ that remains must correspond to well-protected radicals, as indicated by the fact that when DPM$^{\cdot}$ is surrounded by spectator molecules (nondried DPA–NaY composite), the same decay profile is recorded.

In this context, it has been recently reported that oxygen scavenging of benzyl radicals within faujasites can take place distinctively at the stage of primary radical pair, secondary radical pair, or free uncorrelated radicals, depending on the oxygen pressure.[27] Under our experimental conditions, total scavenging of the free benzyl radicals would be expected to take place. Thus, our results suggest that the fast decay in Figure 2B corresponds to the decay of mobile DPM$^{\cdot}$ in the outgassed composite, since a complete scavenging of these species is observed in the presence of oxygen.

In the case of the transient specific to acid zeolites, we studied the influence of increasing methanol adsorption on the rate of decay of the transient at 440 nm on the DPA–HYD composite. Methanol is expected to react with the cation by nucleophilic addition, probably the same reation that occurs with adventitious water in the absence of added scavengers. Adsorption of methanol was carried out by connecting for 15 min an initially evacuated zeolite sample to a deoxygenated methanol reservoir thermostated at 180, 243, and 298 K. Working under these conditions, we observed faster decay traces as the methanol vapor pressure was increased as shown in Figure 9. Higher temperature, 313 K, produced the total disappearance of the 440-nm transient while DPM$^{\cdot}$ monitored at 330 nm was still detectable.

In order to obtain quantitative information about the effect of methanol, a set of rate constants is needed. In this context, it is well established that transient species adsorbed on solid surfaces do not decay in a single exponential manner.[15] We have observed throughout this work that the apparent rate constant depends on

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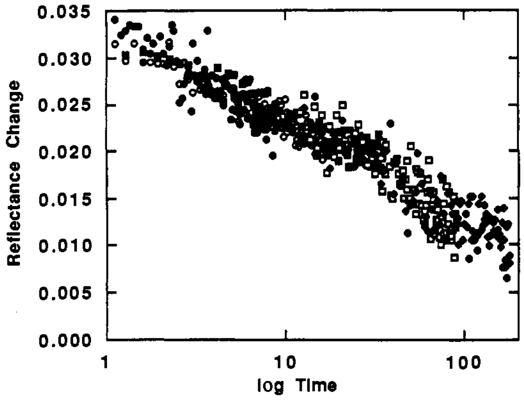


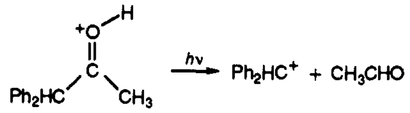
Figure 10. Decay data from traces monitored at 440 nm for DPA–HYD and constructed by combining five experimental traces of different time scales (0.5, 1, 2, 5, and 10 μs).

the time scale monitored, with longer time scales leading to lower rate constants. Therefore, a more precise picture of the 440-nm transient decay requires a stretched trace covering several of the time scales available with our instrument. In Figure 10, we have plotted the signal intensity for the transient on the DPA–HYD complex measured over five different time scales against time.[28] To construct this plot, it was necessary in some cases to normalize traces in the time domain where they overlapped, but the correction was always less than 10%. This type of representation is characteristic of systems that conform to a disperse kinetics type of model,[28] reflecting a distribution of rate constants. An adequate linear representation can also be achieved by plotting ln(signal) against time^x, the best fit in our case corresponding to ln(reflectance change) = −3.16 − 21.76 (time)$^{0.313}$.

A much more simplified presentation of the effect of methanol can be achieved by merely choosing the central portion as representative of the overall stretched decay and treating it with a first-order expression. Thus, the insert in Figure 7 clearly shows that increasing amounts of methanol lead to an acceleration in the decay of the 440-nm transient. Although the results presented in Figure 7 can only be considered as a rough approximation, they provide strong support for methanol quenching of the species characterized by 440-nm reflectance change. As far as we know, this constitutes the first attempt to obtain Stern–Volmer plots within zeolite cavities.[29] While alternative explanations based on some kind of modification of the guest–host interaction by methanol cannot be ruled out, such explanations appear unlikely.

The dependence of the intensity of the 440-nm transient with laser dose was measured using a 308-nm excimer laser as the excitation source and a set of neutral density filters. A good linear relationship between both variables for laser pulses of less than 5 mJ was observed, while a saturation plateau was reached for higher excitation energies. This relationship establishes that the 440-nm transient arises from monophotonic excitation of DPA, thus excluding the implication of excited DPM$^\cdot$ in its formation.[30]

All the above observations are compatible with the 440-nm transient, characteristic of the photolysis on acid faujasites, being DPM$^+$ generated directly from the excited states of the conjugate acid of the starting ketones, eq 3.



(3)

Conclusion

We have demonstrated that the photochemistry of organic guest molecules within zeolite media is determined not only by the topological features of the solid host but can be governed also by the interaction with the charge-compensating cations. Thus, the photochemistry of the phenyl-substituted acetones, DPA and TPA, adsorbed within acidic Y faujasites shows distinctive pathways not observed using the sodium form as the host. We have established that this modification takes place regardless of the acid-strength distribution and the Lewis or Brönsted nature of the zeolite sites and is characterized by the generation of a second transient besides DPM$^\cdot$. The use of a highly dealuminated zeolite with a homogeneous acid-strength distribution results in a remarkably better resolution of the transient spectrum. On the basis of spectroscopic data and methanol quenching experiments and by analogy with independent chemical ionization–mass spectrometry, we assign this new transient as DPM$^+$. Finally, due to the high hydrophilicity of faujasites with a low framework Si/Al ratio, the ability of water readsorbed after inclusion of the organic guest molecule to increase steric congestion and inhibit oxygen quenching has been pointed out.

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(29) Stern–Volmer type plots have been reported on silica gel surfaces. See: Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430–4435.

(30) Conceivably, DPM$^+$ could also be formed by electron transfer from excited DPM$^\cdot$ (see, e.g., ref 31); however, such processes would be nonlinear in laser dose.

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