FINAL REPORT OF RESEARCH SUPPORTED BY
DOE GRANT # DE-FG02-96ER14635

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TITLE: PHOO_ACHEMICAL STUDIES OF TWO COMPONENT SYSTEMS WITHIN THE RESTRICTED
SPACES OF ZEOLITES

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PERIOD: JULY 1996 – JUNE 2001

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A. PUBLICATIONS

Research Papers

1. Selective Oxidation of Olefins within Organic Cation Exchanged Zeolites
X. Li and V. Ramamurthy, *J. Am. Chem. Soc.*, **1996**, *118*, 10666.
2. Triplet-Triplet Energy Transfer Between Organic Molecules Trapped in Zeolites.
K. Pitchumani, J. N. Gamlin, V. Ramamurthy and J. R. Scheffer, *J. Chem. Soc., Chem. Comm.*, **1996**, 2049.
3. An Exceptionally Stable Carbocation from Indene Generated and Trapped within Ca Y Zeolite.
K. Pitchumani and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, **1996**, 2763.
4. Electron Transfer Reactions within Zeolites: Radical Cations from Benzonorbornadiene and Dibenzobarrelene.
K. Pitchumani, D. R. Corbin and V. Ramamurthy, *J. Am. Chem. Soc.*, **1996**, *118*, 8152.
5. Electron Transfer Reactions Within Zeolites: Photooxidation of Stilbenes
X. Li and V. Ramamurthy, *Tetrahedron Letters*, **1996**, *37*, 5235.
6. Cation Radical and Carbocation Mediated Reactions within Ca Y Zeolite: 1-Phenyl 3,4-dihydronaphthalene
K. Pitchumani, P. H. Lakshminarasimhan, G. Turner, M. Bakker and V. Ramamurthy, *Tetrahedron Letters*, **1997**, *38*, 371.
7. Generation and Reactivity of Singlet Oxygen Within Zeolites: Remarkable Control of hydroperoxidation of alkenes
R. Robbins and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, **1997**, 1071.
8. Zeolite as a Reagent and as a Catalyst: Reduction and Isomerization of Stilbenes by Ca Y.
K. Pitchumani, A. Joy, N. Prevost and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, **1997**, 127.
9. Generation, Entrapment and Reactivity of Long Lived Organic Carbocations and Cation Radicals within a Supramolecular assembly: Ca Y zeolite
K. Pitchumani, P. H. Lakshminarasimhan, N. Prevost, D. R. Corbin and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, **1997**, 181.
10. Generation of Stable and Persistent Carbocations From 4-Vinylanisole Within Zeolites

- V. Jayathirtha Rao, N. Prevost, V. Ramamurthy, M. Kojima and L. Johnston, *J. Chem. Soc. Chem. Commun.*, 1997, 2209.
11. Detection Low Levels of Brønsted Acidity in Na⁺Y and Na⁺X Zeolites.
V. Jayathirtha Rao, D. L. Perlstein, R. J. Robbins, P. H. Lakshminarasimhan, H.-M. Kao, C. P. Grey and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, 1998, 269.
 12. Activation Conditions Play a Key Role in the Activity of Zeolite CaY: NMR and Product Studies of Brønsted Acidity
H. M. Kao, C. P. Grey, K. Pitchumani, P. H. Lakshminarasimhan and V. Ramamurthy, *J. Phys. Chem.*, 1998, 102, 5627.
 13. Detection and Estimation of Brønsted Acidities in Alkali Cation exchnaged X and Y Zeolites.
K. J. Thomas and V. Ramamurthy, *Langmuir*, 1998, 14, 6687.
 14. Novel Approaches Towards the Generation of Excited Triplets of Organic Guest Molecules within Zeolites.
K. Pitchumani, M. Warriar, V. Ramamurthy, and J. R. Scheffer, *J. Chem. Soc. Chem. Commun.*, 1998, 1197.
 15. Photoinduced Electron Transfer Reactions Within Zeolites: Detection of Radical Cations and Dimerization of Aryl olefins.
L. Brancaleon, D. Brouismiche, V. Jayathirtha Rao, L. J. Johnston and V. Ramamurthy, *J. Am. Chem. Soc.*, 1998, 120, 4926.
 16. Characterization of persistnt intermediates generated upon inclusion of 1,1-diarylethylenes within CaY: Spectroscopy and Product Studies.
P. Lakshminarasimhan, K. J. Thomas, L. Brancaleon, P. D. Wood, L. J. Johnston and V. Ramamurthy, *J. Phys. Chem., B*, 1999, 103, 9247.
 17. Photo-Fries reactions of 1-naphthyl esters in cation exchanged zeolite Y and polyethylene media.
W. Gu, M. Warriar, V. Ramamurthy and R. G. Weiss, *J. Am. Chem. Soc.*, 1999, 121, 9467.
 18. Understanding the Influence of Active (Zeolite) and Passive (Polyethylene) Reaction Cages on Photo-Claisen Rearrangements of Aryl Benzyl Ethers.
Weiqiang Gu, Manoj Warriar, Brian Schoon, V. Ramamurthy, and Richard G. Weiss, *Langmuir*, 2000, 16, 6977.
 19. Singlet Oxygen Mediated Oxidation of Olefins Within Zeolites: Selectivity and Complexities.

- J. Shailaja, J. Sivaguru, R. J. Robbins, V. Ramamurthy, R. B. Sunoj and J. Chandrasekhar, *Tetrahedron*, **2000**, *56*, 6927.
20. Cation- π Interaction Controlled One-Way Geometric Photoisomerization of Diphenylcyclopropane
P. Lakshminarasimhan, R. B. Sunoj, J. Chandrasekhar and V. Ramamurthy, *J. Am. Chem. Soc.*, **2000**, *122*, 4815.
 21. Cation- π -interaction promoted aggregation of aromatic molecules and energy transfer within zeolites
K. J. Thomas, R. B. Sunoj, J. Chandrasekhar and V. Ramamurthy, *Langmuir*, **2000**, *16*, 4912.
 22. Heavy Cation Effect on Intersystem Crossing Between Triplet and Singlet Phenylacetyl and Benzyl Geminate Radical Pairs Within Zeolites
Manoj Warrier, N. J. Turro and V. Ramamurthy, *Tetrahedron Letters*, **2000**, *41*, 7163.
 23. Configuration Interaction and Density Functional Study of the Influence of Lithium Cation Complexation on Vertical and Adiabatic Excitation Energies of Enones.
R. B. Sunoj, P. Lakshminarasimhan, V. Ramamurthy and J. Chandrasekhar, *J. Comput. Chem.* **2001**, *22*, 1598.
 24. Probing zeolites with organic molecules: Supercages of X and Y zeolites are superpolar.
S. Uppili, K. J. Thomas, E. Crmpton and V. Ramamurthy, *Langmuir*, **2000**, *16*, 265.
 25. Wavelength Dependent Oxygen Mediated Electron Transfer Reactions Within M⁺Y Zeolites: Photo oxidation And Reduction of 1,1-Diarylethylenes
P. Lakshminarasimhan, K. J. Thomas, L. J. Johnston and V. Ramamurthy, *Langmuir*, **2000**, *16*, 9360.
 26. Controlling the Reactive State Through Cation Binding: Photochemistry of Enones within Zeolites
Sundararajan Uppili, Shinsuke Takagi, R. B. Sunoj, P. Lakshminarasimhan, J. Chandrasekhar, and V. Ramamurthy, *Tetrahedron Letters.*, **2001**, *42*, 2079.

Reviews

27. Energy Transfer, Proton Transfer and Electron Transfer Reactions Within Zeolites (Feature article)
V. Ramamurthy, P. Lakshminarasimhan, C. P. Grey and L. J. Johnston, *J. Chem. Soc. Chem. Commun.*, **1998**, 2411-2424.

28. Zeolite as a Medium for Photochemical Reactions
V. Ramamurthy, R. J. Robbins, K. J. Thomas and P. H. Lakshminarasimhan, in '*Organised Molecular Assemblies in the Solid State*', J. K. Whitsell (ed.), John Wiley: Chichester, 1999, pp. 63-140.
29. Zeolite as a spectroscopic matrix.
S. Uppili, P. Lakshminarasimhan and V. Ramamurthy, *IAPS Newsletter*, 1999, 22, 32.
30. Enforcing molecules to behave.
A. Joy, M. Warriar and V. Ramamurthy, *Spectrum*, 2000, 12, issue 3, 1.
31. Controlling Photochemical Reactions via Confinement: Zeolites
V. Ramamurthy, *J. Photochem. Photobiol. C*, 2000, 1, 145-166.

B. RESEARCH PROGRESS

I. INTRODUCTION

In this section a brief summary of the research progress made during the last two and half years are summarized. The goal of this study has been to establish the utility of zeolite as a medium to conduct highly selective photochemical reactions. In the process we discovered that zeolite as a medium is complex and several properties of zeolite that might interfere with photochemical reactions need to be understood. During the first phase of the project we have made progress towards understanding zeolite as a medium and also have established with a few examples that reactions conducted within a zeolite can be highly selective. For details one should refer to scientific publications which are listed in the previous section.

II. PROTON TRANSFER REACTIONS WITHIN ZEOLITES

A side reaction initiated by a proton transfer process complicated our observations during our investigation of olefins within zeolites. This prompted a mechanistic study of proton transfer reactions within zeolites. This study included isolation of products, characterization of intermediates and estimation of acidic sites within monovalent and divalent cation exchanged zeolites. Results of these investigations, some of which have been published, are briefly summarized in this section.^{1,2}

II. A. CHARACTERIZATION OF PRODUCTS AND PERSISTENT CARBOCATIONS

Inclusion of olefins: indene, vinyl anisole and 1,1-diphenylethylene within activated (500°C oven), normally white Ca Y zeolite resulted in bright coloration of the zeolite which persisted for several weeks even after extraction of the products (Figures 1-4). The products isolated from these colored zeolites are listed in Schemes 1, 2 and 3. An initial protonation of the olefin by the Brønsted acid sites that are present in an activated CaY would rationalize the derivation of the isolated products (Scheme 4). Studies using perdeuterated hexane and D₂O exchanged Ca Y

indicated that the proton came from the acidic sites present in the zeolite, and the hydride from the solvent hexane.

Figure 1: Persistent colors that result upon inclusion of the three olefins within activated (500°C, oven) Ca Y.

Scheme 1

Scheme 2

Scheme 3

Figure 2: Diffuse reflectance spectrum of the CaY sample loaded with indene. The absorption at 520 nm is due to a dimeric allylic cation.

Figure 3: Diffuse reflectance spectrum of the CaY sample loaded with vinyl anisole. The absorption at ~570 nm is due to a dimeric allylic cation. The species (monomer cation) responsible for absorption at ~350 nm can be washed away with solvent.

Figure 4: Diffuse reflectance spectrum of the CaY sample loaded with diphenyl ethylene. The absorption at ~610 nm is due to a dimeric allylic cation. The species (monomer cation) responsible for absorption at ~420 nm can be washed away with solvent.

Scheme 4

A common feature of these three olefins is the generation of a strongly colored, persistent species within CaY. The most challenging aspect of this study was the identification of the species responsible for the color within the zeolite. Indene has been reported in the literature to develop color in presence of Lewis acids.³ This red color is attributed to carbonium ion **1** formed from 2- α -indanylindene (**2**, Scheme 5) by abstraction of a hydride. We believe that the red color and the absorption maximum at ~520 nm within Ca Y is due to the same cation as the one in solution. The cation **1** is stable for a few seconds only under degassed conditions in solution, but within a zeolite this cation is stable for an extremely lengthy period. We suggest that the red-violet color seen in the case of 4-vinyl anisole is due to a similar allylic cation **3** formed from **4** (Scheme 6). The proposed sequence of steps that lead to the two persistent cations **1** and **3** are shown in Schemes 5 and 6.

Scheme 5

The greenish blue coloration of diphenyl ethylene that we observed in zeolites has been reported earlier in other media (in liquid acid media as well as on silica-alumina surfaces).⁴ In the past, several suggestions have been made for the coloration (Scheme 7). One proposal is that the color is due to a monomer radical cation (**6**).^{4b-e,5} In order to provide confirmatory evidence we needed the absorption spectrum of the diphenylethylene radical cation. A number of groups have reported widely varying absorption characteristics of the diphenyl ethylene radical cation.⁶ Our attempts to record the spectrum for the radical cation of diphenyl ethylene have thus far been unsuccessful. However, the spectra we have obtained for the radical cations of 1,1-diphenyl

1-propene and 1,1-diphenyl, 2-methyl-1-propene both in solution and within zeolites show absorption at 400 nm and at wavelengths past 700 nm (Figure 5). Our expectations for the radical cation of diphenyl ethylene to absorb in the same region as the above two analogous cation radicals ruled out the possibility of the blue species being this radical cation (6).

Scheme 6

Scheme 7

We then turned our attention to the dimer cation 9.⁴ⁱ We generated the cation from the two precursors shown in Scheme 8. The spectra recorded are provided in Figure 6. Clearly the same primary cation with an absorption maximum at 430 nm is generated from both precursors. The observed absorption maximum is consistent with that expected of a diphenyl alkyl cation and not that of an allylic cation.⁷ We conclude that the absorption recorded soon after inclusion of the olefin (10) and the alcohol (11) into activated Ca Y is due to the dimer cation (9) which does not

have an absorption, as expected, in the region above 500 nm. This led us to explore the possibility of a dimeric allylic cation, similar to the ones obtained in the case of indene and vinyl anisole as an intermediate responsible for the blue color (Schemes 5 and 6). Our view that a dimeric allylic cation might be responsible for the color is supported by the following observation: Cations of end capped diphenyl ethylenes, 1,1-diphenyl 1-propene and 1,1-diphenyl 2-methyl-1-propene, would not be expected to dimerize within the confined spaces of a zeolite supercage and should therefore show no absorption due to the dimeric allylic cation. These two olefins gave a yellow color on contact with Ca Y, an exclusive result of the monomeric cation.

Figure 5: Transient absorption spectra of the 1,1-diphenyl-2-methyl propene radical cation in acetonitrile.

Scheme 8

Figure 6: Diffuse reflectance spectra of the dimer cation **9** generated from the precursor olefin and alcohol with activated Ca Y.

An important difference between vinyl anisole, indene and diphenylethylene is the fact that while the first two olefins can readily yield alkenes containing an allylic hydrogen (see structure **2** in Scheme 5 and **4** in Scheme 6) as the precursor for an allylic cation, diphenylethylene can not do so without migration of either a phenyl or a methyl group. One could visualize the allylic cations **7** and **17** as possible intermediates responsible for the absorption at 615 nm (Scheme 9). Both structures require the formation of alkenes with allylic hydrogen (**15** in the case of **17** and **16** in the case of **7**). Formation of these olefins requires an unusual step namely the formation of less stable cation **12** from more stable cation **9** (Scheme 9). Once **12** formed, it is likely to undergo rearrangement via migration of either a phenyl or methyl group (Scheme 9) to more stable cations **13** and **14** respectively. The driving force for formation of **12** from **9** may come from the non-classical nature of **12** shown in Scheme 10. Formation of dimer allylic cations **7** and **17** from the precursor alkenes **16** and **15** would be anticipated based on the behavior of vinylanisole and indene within CaY. We suggest that the blue color of CaY is due to these allylic cations. Thus the behavior of all three olefins are consistent with each other. At this stage we are unable to provide additional firm evidence to support the above suggested intermediates (**7** and **17**). We have not

isolated either 15 or 16 as products. We also could not synthesize the precursors of 7 and 17 to unequivocally confirm the absorption characteristics of the suspected cations. The extraordinary stability of the carbocations 1, 3 and 7/17 derives partly from π -conjugation with the aromatic substituents. This kinetic stability must be augmented by the highly polar nature of the zeolite supercage. The cations that are generated serve as counter ions for the zeolite framework and thus become integral part of the zeolite structure.

Scheme 9

Scheme 10

The unusual ability to stabilize certain carbocations within zeolites has allowed us to handle them as 'normal' laboratory chemicals. For example, we have been able to record emission from several of these cations one of which is provided in Figure 7.

Figure 7: Emission spectra of the monomer and dimer allylic cations trapped within Ca Y zeolite. Spectra recorded at room temperature.

II. B. PROBING ZEOLITES FOR BRØNSTED ACIDITY: INDICATOR METHOD

During the course of our investigation with olefins we realized that it is important to characterize the zeolite for Brønsted acidity. Two approaches were used: MAS NMR and indicator color method. The former method worked best with highly acidic zeolites and the latter method with modestly or weakly acidic zeolites. Characterization of highly acidic Ca Y by MAS NMR technique was conducted in collaboration with Dr. C. Grey of State University of New York, Stony Brook. A publication in *J. Phys. Chem.* presents our results in detail.¹ Results on monovalent cation exchanged zeolites, often considered being non-acidic, are briefly summarized here.⁸ Based on NMR studies it was concluded that the number of Brønsted acid sites within Na Y must be beyond the detection limits of this technique. We therefore employed a different technique to detect the acidic sites within zeolites. This involved detecting differences in

electronic absorption characteristics between protonated and unprotonated forms of a probe molecule.^{2b}

The critical aspect of the technique was to find a dye molecule that would exhibit different colors under acidic and basic conditions and easily fit within a zeolite. A set of probe molecules, which we have used, is listed in Scheme 11. Cyanine dyes 20-22 listed in Scheme 11 are brightly colored under basic or neutral conditions and turn colorless under acidic conditions. Two probes—retinol and retinyl acetate (18 and 19) are blue under acidic conditions and light yellow under basic/neutral conditions. The preliminary test consisted of monitoring the absorption changes upon addition of a small amount (50 to 200 mg) of an activated zeolite to a standard micromolar hexane solution (5 mL) of the dye. When activated Na Y was added to a standard solution of retinol or retinyl acetate, the zeolite immediately turned dark blue. The color persisted for nearly an hour. This observation was interpreted to mean that Na Y contains Brønsted acidic sites that are strong enough to protonate retinol and retinyl acetate. Consistent with this was the observation with cyanine dyes (Scheme 11). On addition of the dye to activated Na Y, the bright color of the dye faded and the zeolite remained white. Na X did not show a positive blue test with either retinol or retinyl acetate or decolorized cyanine dyes. This led us to conclude that Na X is less acidic than Na Y.

Scheme 11

The number of Brønsted acid sites present was estimated by a conventional titration method. n-Butyl amine, diethyl amine or pyridine was used as a base to quench the acidic sites present in a zeolite. A schematic illustration of the titration method is shown in Scheme 12.

Scheme 12

A typical experimental protocol involved stirring of a known amount of Na Y with varying amounts of the base. After at least 6 hrs of stirring the indicator dye was added and the visible color change was either observed or recorded. Surprisingly, when the base was present in amounts exceeding 1 molecule per 16 cages retinol and retinyl acetate did not turn blue. The cyanine dyes likewise maintained their bright colors without fading. This indicated to us that there must not be more than one acidic site per 16 supercages in Na Y. Although this number is small it is effective enough to bring about changes in the structure of the guest olefins by a catalytic process. We have found that Na Y neutralized with small amounts of a base such as pyridine or diethyl amine can be safely used as a medium for photoreactions without complications from Brønsted acid sites.

III. ELECTRON TRANSFER WITHIN ZEOLITES

Zeolite, in addition to being a good proton source, is also known to accept and donate electrons. This feature complicates the observed chemistry of included guest molecules. We therefore felt that it is important to characterize the electron transfer feature of a zeolite. In this context we have employed 1,1-diarylethylenes as probes. Results obtained with these probes within a zeolite have provided an insight into the electron transfer process within a zeolite.⁹

The products of direct excitation of hexane slurry of di (4-methoxyphenyl) ethylene and 1,1-diphenylethylene included within Na Y zeolite are shown in Schemes 13 and 14 respectively. The ratio of the products of oxidation to reduction was dependent on the wavelength of excitation. More importantly, no products were formed by excitation at any wavelength on excluding oxygen from the system. The key intermediate during both the reduction and the oxidation processes is believed to be the radical cation of diarylethylene formed via an electron transfer process.

Scheme 13

Scheme 14

A transient diffuse reflectance study of Na Y zeolite samples (308 nm excitation) carried out in collaboration with L. Johnston (NRC, Ottawa) confirmed the formation of radical cations via photoionization of di(4-methoxyphenyl)propene and di(4-methoxyphenyl)2-methyl propene. Diffuse reflectance spectra of the respective radical cations were recorded when the olefins were excited with a 308 nm laser. Direct excitation of the olefins, even in the absence of oxygen, resulted in radical cations, suggesting that the primary process does not involve oxygen. The first step is believed to be the ejection of an electron by the excited olefin. The ejected electron is then most likely trapped by Na^+ ions to form Na_4^{3+} clusters. The absorption spectrum, with a maximum at 500 nm due to the trapped electron, was recorded. The presence of oxygen quenches the absorption due to the trapped electron without affecting the spectrum of the olefin radical cation. Based on the above observations we believe that direct excitation (with light of wavelengths below 300 nm) of diarylethylene included within Na Y results in photoionization to yield the radical cation.

Excitation of the olefin with longer wavelength light (>350 nm) leads to a different mechanism. Frei and co-workers have extensively investigated the formation of hydrocarbon-oxygen complexes within zeolites.¹⁰ The diffuse reflectance spectrum recorded by H. Frei and S. Vasenkov for us (Figure 8) indicates that di(4-methoxyphenyl)ethylene forms an oxygen complex when present within Na Y. Longer wavelength light excites the olefin-oxygen complex and an electron transfer occurs within the complex. The proposed mechanisms for the formation of products upon short and long wavelength excitations are shown in Scheme 15. Electron transfer

is considered to be the primary step under both conditions. While the role of oxygen during oxidation is easily understood, its role during the reduction of olefins is less clear. A tentative proposal is that oxygen helps to slow the back electron transfer process.

Figure 8: Diffuse reflectance spectra of 4,4'-dimethoxydiphenylethylene included within Na Y. The bottom spectra is in presence of 800 Torr oxygen. The other two are controls. (Spectra recorded by H. Frei and S. Vaenkov).

In the absence of oxygen the olefin radical cation and the Na_4^{3+} clusters presumably are present in the same cage. Under these condition the back electron transfer process might compete effectively with the reduction process. On the other hand, oxygen can quench the Na_4^{3+} clusters and in the process the electron will be moved farther away. This is schematically illustrated in Scheme 16. The electron transfer mediated oxidation and reduction of 1,1-diphenylethylene described above were established to be general by examining the behavior of several olefins (Scheme 17). Expectedly, upon irradiation, NaY included olefins listed in Scheme 17 gave products resulting from both oxidation and reduction.

Scheme 15

Scheme 16

Scheme 17

IV. ORIGIN OF FACILE PROTON AND ELECTRON TRANSFER WITHIN ZEOLITE: ZEOLITE AS A SUPER-POLAR MEDIUM

Zeolite is an unusual medium of choice for conducting photochemical reactions. As discussed above zeolite can participate in reactions serving as proton donors and as electron acceptors. While these features could complicate the desired results, zeolite possesses certain unique features not found in other organized media. For example, the interior of a zeolite is known to possess very high electric field.¹¹ This property has been utilized by Frei and co-workers in their investigation of the oxidation of alkenes and alkanes within a zeolite. The generation of acidic sites within divalent cation exchanged zeolites, discussed in a previous section, is in fact a direct result of the high the electric field present in a supercage. One of our

primary interests is to modify the photochemical behavior of olefins through the use of electric field (see next section). This interest led us to gain qualitative information on the field within a zeolite supercage. In a qualitative sense micropolarity and electric field may be viewed as different manifestations representing the same property of a medium. We recognize that the micropolarity as monitored by organic probes is only an average number and may not be an accurate representation of the polarity of the supercage. Scheme 18 lists the organic photophysical probes that were used by us. Results with these probes led to similar conclusions, though we briefly summarize below the results with Nile Red only. A manuscript summarizing these results is ready for submission to Langmuir.¹²

Scheme 18

Since the absorption and fluorescence emission maxima and the excited singlet lifetime of Nile Red depend on the polarity of the medium (Table 1), Nile Red seemed like an ideal probe to monitor the micropolarity of the zeolite environment. A comparison of the photophysical behavior and spectral characteristics of Nile Red in solution and in zeolites suggested that the zeolite interior is more polar than a water-methanol mixture. The micropolarity of the interior depends on the cation, with a smaller cation leading to greater micropolarity. Even Cs Y is found to be more polar than a 60% water-methanol mixture. The linear relationship observed between the absorption maxima, singlet lifetime and the cation size (Figures 9 and 10) suggests an important role for the cation in influencing the micropolarity of the supercage. When the zeolite interior is 'wet' (filled with water), the micropolarity, expectedly, decreases (Figure 11). The micropolarity sensed by Nile Red under such conditions is in fact similar to that of water. Based on micropolarity readings obtained with Nile Red as the probe, we conclude that zeolite Y is

more polar than zeolite X (Figure 12). This observation is consistent with literature information on electric fields within X and Y zeolites.¹¹ Identical conclusions were drawn with the other probes listed in Scheme 18.

Table 1: Solvent Dependent Photophysical properties of Nile Red

Solvent	Abs. Max.	Em. Max.	τ_1 (ns)
Benzene	524	575	6.84
CH ₂ Cl ₂	538	605	4.21
MeOH	552	642	2.61
40% H ₂ O/ MeOH	575	655	1.29
60% H ₂ O/ MeOH	584	660	-

Figure 9: Cation dependence of absorption maximum of the probe 'nile red' included within M⁺ Y zeolite.

Figure 10: Cation dependence of fluorescence lifetime of the probe 'nile red' included within M^+ Y zeolite.

Figure 11: Micropolarity dependence, as probed by 'nile red', on water content within M^+ Y zeolite.

Figure 12: Micropolarity dependence, as probed by 'nile red', on the number of cations within a zeolite, X vs. Y zeolite.

V. SELECTIVE OXIDATION OF OLEFINS WITHIN ZEOLITES: FEASIBILITY OF ENERGY TRANSFER AND POLARIZATION OF OLEFINS

Singlet oxygen is known to react with electron rich olefins via a [2+2] addition process.¹³ However, when the olefin contains allylic hydrogens the 'ene reaction' predominates. Olefins with more than one distinct allylic hydrogen yield several hydroperoxides (Scheme 19). With a medium such as zeolite, that is studded with cations, we envisioned that it should be possible to achieve high selectivity during singlet oxygen ene reaction and we have achieved this goal with several olefins of which the results obtained with 1-methylcyclooctene are presented in this section. Two communications have been published and full papers are under preparation.¹⁴

Scheme 19

Oxidation of olefins with singlet oxygen requires assembling oxygen, olefin and a sensitizer—within the internal structure of a zeolite.¹⁵ Thionin was easily exchanged into Na Y zeolite by stirring the dye with hydrated Na Y in water. While the exchanged dye remains in a dimeric form within hydrated Na Y, careful drying results in a color change accompanied by thionin adopting a monomeric structure (Figure 13). The monomeric thionin is a sensitizer useful for the generation of singlet oxygen. Excitation of a blue zeolite containing monomeric thionin shows an emission from singlet oxygen. Reactivity of singlet oxygen was tested with several olefins listed in Scheme 20. 2,3-Dimethyl 2-butene and 2-methyl 4,4-dimethyl 2-pentene were oxidized to the corresponding hydroperoxides (Scheme 20) within thionin-Na Y. These products are the same ones obtained during singlet oxygen oxidation in solution. 1,2-Dimethylcyclohexene was used as a chemical probe to further establish the nature of the oxidising species. As a result of oxidation this olefin gives three three peroxides. But the ratio of the three peroxides is dependent on the nature of the oxidant, singlet or triplet oxygen (Scheme 20). The product distribution obtained within thionin exchanged zeolite is nearly identical to that obtained during singlet oxygen oxidation of 1,2-dimethylcyclohexene in acetonitrile. The above results support the conclusion that a reactive singlet oxygen can be generated within the confines of a

zeolite and sets the stage for us to explore the initial goal of achieving selectivity during the ene reaction.

Figure 13: The diffuse reflectance spectra of thionin included within NaY. The dry and wet samples show different spectra and differently colored.

Scheme 20

Of the many olefins (Scheme 21) we examined, results obtained with 1-methylcyclooctene, are presented below. Other olefins in Scheme 21 showed similar product selectivity. 1-Methylcyclooctene possesses three allylic hydrogens and therefore three hydroperoxides are expected (Scheme 22). All three hydroperoxides are formed during singlet oxygen oxidation in acetonitrile solution. On the otherhand, when the oxidation was conducted within Na Y-thionin a single hydroperoxide was identified by GC (Figure 14). The selectivity obtained within the zeolite is clearly remarkable. The question whether the observed selectivity is due to selective destruction of one or more of the products has been addressed. The following control ensured that the observed selectivity is not an artifact: The product hydroperoxides and alcohols were independently synthesized from rose bengal sensitized oxidation of 1-methylcyclooctene in acetonitrile and were introduced into NaY-thionin and tested for stability. All three hydroperoxides and alcohols from 1-methylcyclooctene were stable within the zeolite and were extracted without much loss.

Olefins tested inside M⁺ Yzeolite for selectivity

Scheme 21

Scheme 22

Figure 14: The GC trace of the oxidation products of 1-methylcyclooctene in solution (bottom) and within zeolites. Note within NaY zeolite only one product is obtained. The product peaks are in the same order as in Scheme 22 (from left to right).

We attribute the selectivity to the polarization of the olefin by cations present within a supercage. Two approaches—theoretical calculations and MAS NMR—are being taken in pursuit of evidence in favor of cation-olefin interactions. The former study is being carried out in collaboration with J. Chandrasekar of IISc, Bangalore and the latter with C. Grey of SUNY, Stonybrook. Ab initio calculations (by MP2, B3LYP and HF methods) suggest that cations do bind with significant binding energies to the olefin π -cloud (gas phase). As expected the binding energy shows an inverse relationship with the size of the cation (Scheme 23). It also indicated that the HOMO of an unsymmetrical olefin is polarized by the cation (Figure 15). Based on the above theoretical reasoning 1-methylcyclooctene can also be expected to be polarized within a zeolite cage. Under such conditions, we expected that the electrophilic singlet oxygen to attack the electron rich carbon (δ^-) the one without the methyl substituent. Such an attack would lead to an ene reaction in which hydrogen abstraction will occur selectively from the methyl group

connected to the carbon bearing δ^+ . Further we believed that selectivity would depend upon the extent of polarization. Smaller cations such as Li^+ would be expected to polarize the olefin more than larger cation such as Cs^+ . As per this model selectivity is expected to decrease from Li^+ to Cs^+ . Consistent with the above model, the observed selectivity did decrease with the size of the cation ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$) (Scheme 24).

Figure 15: Electron density at the HOMO orbital of 2-methyl-2-propene plotted with Molden program and calculated by *ab-initio* method. (a) free molecule, (b) in presence of Li^+ and (c) in presence of Be^{2+} .

CONCLUSIONS

During the last three year period we have explored the use of zeolites to carry out selective phototransformations. We have shown that it is possible to carry out selective oxidation of olefins within zeolites. Cations within zeolites are unique and they interact with olefins and polarize the HOMO orbitals. The use of zeolite as a reaction medium requires an understanding of the zeolite itself. We have used several organic molecules to probe the proton and electron transfer properties of zeolites. We feel that the stage is ideally set to exploit zeolites as media for conducting selective phototransformations.

VI. REFERENCES

1. V. Ramamurthy, P. Lakshminarasimhan, C. P. Grey and L. J. Johnston, *J. Chem. Soc. Chem. Commun.*, 1998, 2411-2424.
2. (a) H. M. Kao, C. P. Grey, K. Pitchumani, P. H. Lakshminarasimhan and V. Ramamurthy, *J. Phys. Chem.*, 1998, 102, 5627. (b) K. J. Thomas and V. Ramamurthy, *Langmuir*, 1998, 14, 6687. (c) P. H. Lakshminarasimhan, K. J. Thomas, L. Johnston and V. Ramamurthy, *J. Phys. Chem.*, submitted.
3. H. J. Prosser, R. N. Young, *European Polym. J.* 1972, 3, 879.
4. (a) A. G. Evans, P. M. S. Jones and J. H. Thomas, *J. Chem. Soc.* 1957, 104. (b) H. P. Leftin, and W. K. Hall *J. Phys. Chem.* 1960, 64, 382. (c) H. P. Leftin, *J. Phys. Chem.* 1960, 64, 1714. (d) H. P. Leftin, and W. K. Hall, *J. Phys. Chem.* 1962, 66, 1457. (e) H. P. Leftin, M. C. Hobson and J. S. Leigh, *J. Phys. Chem.* 1962, 66, 1214. (f) J. J. Rooney and R. C. Pink, *Trans. Faraday Soc.* 1962, 1632. (g) W. K. Hall, *J. Catalysis* 1962, 1, 53. (h) F. R. Dollish and W. K. Hall, *J. Phys. Chem.* 1965, 69, 4402. (i) V. Fornes, H. Garcia, S. Jovanvic and V. Marti, *V. Tetrahedron*, 1997, 53, 4715.
5. K. Pitchumani, P. H. Lakshminarasimhan, N. Prevost, D. R. Corbin and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, 1997, 181.
6. (a) H. Al-Ekabi, H. Kawata and P. de Mayo, *J. Org. Chem.* 1988, 53, 1471. (b) T. Shida and W. H. Hamill, *J. Chem. Phys.* 1966, 44, 4372. (c) O. Brede, J. Bos, W. Helmstreet and R. Mehnert, *Radiat. Phys. Chem.* 1982, 19, 1. (d) K. Mizuno, T. Tamai, I. Hashida, Y. Otsuji, Y. Kuriyama and K. Tokumaru, *J. Org. Chem.* 1994, 59, 7329. (e) S. Konuma, S. Aihara, Y. Kuriyama, H. Misawa, R. Akaba, H. Sakuragi and K. Tokumaru, *Chem. Lett.* 1991, 1897.
7. (a) J. Sonderrmann and H. Kuhn, *Chem. Ber.*, 1966, 99, 2491. (b) R. N. Young, B. Brocklehurst and P. Booth, *J. Am. Chem. Soc.*, 1994, 116, 7885. (c) R. A. McClelland, C. Chan, F. Cozens, A. Modro and S. Steenken, *Angew. Chem. Int. Ed. Engl.*, 1991, 30, 1337. (d) R. A. McClelland, V. M. Kangasabapathy and S. Steenken, *S. J. Am. Chem. Soc.* 1988,

- 110, 6913. (e) A. Azarani, A. B. Berinstain, L. J. Johnston and S. Kazanis, *J. Photochem. A: Chem.* **1991**, *57*, 175.
8. V. Jayathirtha Rao, Deborah L. Perlstein, Rebecca J. Robbins, P. H. Lakshminarasimhan, Hsein-Ming Kao, Clare P. Grey and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, **1998**, 269.
 9. P. H. Lakshminarasimhan, K. J. Thomas, L. Johnston and V. Ramamurthy, *J. Phys. Chem.*, Submitted.
 10. H. Frei, F. Blatter and H. Sun, *Chemtech.*, **1996**, *26*, 24.
 11. (a) J. A. Rabo, *Cat. Rev. -Sci. Eng.*, **1981**, *23*, 293. (b) E. Dempsey "Molecular Sieves" Society of Chemical Industry, London, **1968** p. 293. (c) E. Preuss, G. Linden and M. Peuckert, *J. Phys. Chem.*, **1989**, *89*, 2955.
 12. K. J. Thomas, S. Upplili, E. Crompton and V. Ramamurthy, *Langmuir*, submitted.
 13. (a) *Singlet Oxygen*, H. H. Wasserman, R. W. Murray, (Eds.), Academic Press:New York, **1979**, (b) *Singlet Oxygen*, Vols. 1-4, A. A. Frimer, (Ed.), CRC Press: Boca Raton, **1985**.
 14. X. Li and V. Ramamurthy, *J. Am. Chem. Soc.*, **1996**, *118*, 10666.
 15. R. Robbins and V. Ramamurthy, *J. Chem. Soc. Chem. Commun.*, **1997**, 1071.