

Photochemical processes in zeolites: new developments

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Abstract

The organized channels and cages of zeolites provide a novel medium for carrying out photochemical reactions. Besides the confinement effect, the role of zeolite framework, extra-framework cations and the unique solvent nature of the zeolite all have profound influence on the photochemistry and photophysics of molecules. In this review, we have highlighted the important developments in the field of zeolite photochemistry over the past two years. Examples of photochemical reactions, photooxygenations and photoelectron transfer are presented. In addition, there has been considerable interest in using zeolite-based photochemistry for environmental remediation. Novel zeolitic materials, including zeolite composites, sensors and multifunctional assemblies that use light to initiate function are also described.

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1. Introduction

Zeolites are microporous crystalline aluminosilicates with structural features that make them attractive hosts for photochemical applications. Extra framework cations necessary for charge neutralization can interact with guest molecules. Zeolite cages and channels are of the order of 4–14 Å, and molecular confinement can alter photochemical reactivity. Intracrystalline zeolite space is also a novel “solvent”. This review covers the literature in the area of zeolite photochemistry and photophysics over the past two years and is divided into photochemical reactions, photooxygenation reactions, photoelectron transfer processes, photochemically driven environmental remediation, novel photochemical materials and sensors and multifunctional assemblies in zeolites.

Over a dozen review articles have appeared in the literature in zeolite photochemistry over the past two years in the following areas:

- photophysical probes of the interior surfaces of zeolites [1],
- role of extra-framework alkali and heavy metal cations on photochemistry [2],

- chiral induction and stereochemical control of photo-reactions [3],
- selectivity of photooxidation of organics by molecular oxygen [4],
- use of transient spectroscopic studies for organic reaction mechanisms [5],
- ability of zeolites to stabilize unstable organic radical ions [6],
- comparison of zeolites with supports such as Nafion and microemulsions [7],
- photodegradation of both organic and inorganic pollutants [8],
- NO_x decomposition and carbon dioxide activation and other photocatalytic reactions using transition metal oxides within the zeolite framework [9–11],
- assembly of organic molecules to make antenna systems for light harvesting [*12,13],
- novel ways of introducing organic molecules in zeolites so that the chemical degradation is minimized [14],
- quantum dot materials involving compounds of copper, silver, and gold [15].

Three book chapters that provide exhaustive reviews of photochemical reactions, photoelectron transfer and novel optical materials in zeolites have recently appeared in the *Handbook of Zeolite Science and Technology* [*16,*17,*18]. A fourth detailed review article

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about aspects of electron transfer in zeolites and mesoporous materials is also worth consideration [19].

2. Zeolites as photoreactors

The photochemistry of organic molecules in zeolites continues to be of interest. Upon photoexcitation of biphenyl in zeolite X, the triplet state, radical cation, and radical anion of biphenyl was formed. At low light fluence, the triplet state was the major transient species, with lifetimes of 100 μ s. With high laser fluence, photoionization of biphenyl occurred with the photoejected electrons being trapped as extra-framework Na_4^{3+} clusters. The anion radical found at high loadings was formed by capture of the photoejected electron by biphenyl molecules [20].

Anils in zeolite Y were found to exist primarily in the zwitterionic form. Steady state irradiation led to photochemical *anti-syn* isomerization of the zwitterions around the C–C or C–N bonds, a feature not observed in solution or in the crystalline form [21].

It has been reported that C_{60}^- formed spontaneously in zeolites, the amount of C_{60}^- being considerably higher in Na–Y as compared to Na–X, presumably due to the higher polarity in Na–Y. However, the lower yield of the anion in Na–X could also arise from the higher framework negative charge. In both zeolites, C_{60} and C_{60}^- exhibit considerably longer excited state lifetimes, explained as arising due to lack of collisions upon zeolite confinement [22]. Another anion (3-ethylphenyl)phenylmethanone, generated from ketoprofenate was found to have long excited state lifetime in Na–Y. Intrazeolitic nucleophilic reactions of the anion with acetaldehyde and other reagents were demonstrated [23].

The photochemical properties of 2,3-diazabicyclo[2.2.2]oct-2-ene (dbo) has been studied in zeolite Y, mordenite, ZSM-5, and HZSM-5, as well as mesoporous MCM-41, silica, silica-alumina and γ -alumina. The quenching of photoexcited dbo by oxygen was strongly dependent on the host zeolite and dependent on the hydroxyl groups (water) in the framework [24].

Silver ion exchanged ZSM-5 was found to contain Ag_m^{n+} clusters. UV irradiation (285 nm) at 77 K led to formation of $\text{Ag}_m^{(n-1)+}$, with the zeolite framework acting as the electron donor. The reduced silver cluster exhibited a bright blue luminescence. Molecular oxygen competed effectively with Ag_m^{n+} as the electron acceptor [25].

Molecules such as ethylene in dehydrated zeolites react under visible light illumination. Based on calculations, it has been proposed that the reason for reactivity is because of charge transfer transitions from the ethylene HOMO to the zeolite framework which extend into the visible region [26].

Typical ways to introduce organic molecules in zeolites are via vapor phase or through a solvent, limiting

the size of the molecule that can be introduced. Several ship-in-a-bottle type of synthesis of larger molecules in zeolite Y, including a bipyrylium ion which occupies two supercages [27] and cyclobis (*N,N'*-paraquat-*p*-phenylene) macrocycle ($2^{4+}@Y$), which is the electron acceptor component of rotaxanes and catenanes has been reported [28]. Strategy for synthesis of $2^{4+}@Y$ is shown in Fig. 1. Photoelectron transfer between charge-transfer complexes of $2^{4+}@Y$ and 1,4 dimethoxybenzene (DMB) led to formation of transients having lifetimes of hundreds of microseconds, as contrasted to acetonitrile, where no transients were detected on the nsec time scale.

The photochemistry of benzil on flexible *p*-tert-butylcalix[*n*]arene ($n = 4, 6$ and 8) was compared with that on the hydrophobic, rigid zeolite, silicalite. The calixarenes tended to provide longer excited state lifetime for benzil. However, triplet-triplet absorption of benzil was more pronounced in silicalite [29]. The photochemistry of 4-chlorophenol has also been compared between silicalite and β -cyclodextrin. Transient spectroscopy showed the formation of the phenoxyl and 4-chlorophenoxyl radical in cyclodextrin and only the latter in silicalite. Photodegradation products were phenol in cyclodextrin, and in silicalite, the products were formed by ring cleavage [30]. Photochemistry of benzophenone was compared between *p*-tert-butylcalixarene, silicalite, and microcrystalline cellulose. Silicalite showed the highest phosphorescence quantum yield and lifetime with a distorted benzophenone molecule. In silicalite, only triplet-triplet transient absorptions of the ketone were observed, whereas in cellulose and calixarenes, H abstraction led to the formation of ketyl radicals [31].

Typical methods to generate triplets of organic molecules in zeolites involve heavy atom effect and sensitization. Interestingly, in some cases, even lithium and sodium ions in zeolite can influence triplet yield by selective π -interactions, as noted for the Zimmerman rearrangement of dibenzobarrelene [32]. Another example

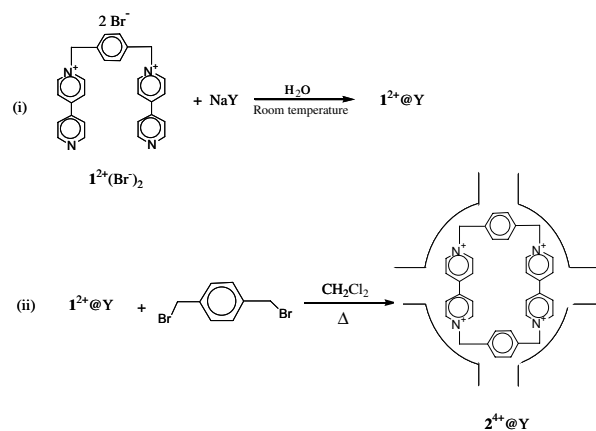


Fig. 1. Strategy for intrazeolitic synthesis of cyclobis (*N,N'*-paraquat-*p*-phenylene) macrocycle ($2^{4+}@Y$) (reprinted from Ref. [28]).

of how cation binding alters photochemistry is the geometric isomerization of photoexcited 1,2-diphenylcyclopropane. The *cis*- to *trans*-isomerization is not observed in the zeolite because of cation binding to the *cis*-phenyl groups. If the ester or amide derivative of the cyclopropane was examined, then the cation binding shifted to the carbonyl group, and isomerization was observed [33].

The yield of the carbocation formed by the C–O photoheterolytic bond cleavage of 9-cyclopropyl-9-fluorene (CF) was dependent on the Lewis acidity of the extra-framework cations. The decay of the CF ion was proposed to occur via nucleophilic attack of the Si–O–Al bridges of the zeolite framework [34].

Control of the extent of chirality was compared between reactions occurring in a zeolite and on an ionic crystal. The diastereomeric excess in the *cis*- to *trans*-photoisomerization of derivatives of *trans trans* 2,3-diphenyl-1-benzoyl-cyclopropane was found to depend upon the cation and levels of asymmetric induction reached as high as 71% using chiral auxiliaries [35].

Fluorescence microscopy has been used to investigate migration of molecules between zeolites crystallites separated from each other and in contact. Phenanthrene and chrysene migrated preferentially from Na–X to Tl–X, demonstrating the importance of the cation. Formation of charge transfer complexes between donor molecules phenanthrene and chrysene in a zeolite particle and acceptor 1,2,4,5-tetracyanobenzene in a separate zeolite particle also facilitated migration, via motion of only the donor molecules [36].

3. Photoelectron transfer

Electron transfer reactions within zeolites and from zeolites to external electron donors and acceptors continue to be an active area of research, and the zeolite framework is emerging as a major participant in the electron transfer process. The extent of photoionization of methyl viologen (MV^{2+}) showed that the viologen radical yield increased as follows $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, all in zeolite X. This order reflects the partial charges on the oxygen atoms of the framework [37]. With Cr(V) exchanged zeolite X, EPR spectroscopy confirmed that Cr(V) acts as the electron acceptor for photooxidation of *N,N,N',N'*-tetramethylbenzidine. The zeolite was more efficient in generating the benzidine radical cation as compared to silica gel, zirconium phosphate, mordenite, and silicoaluminophosphates [38].

Electron transfer through the zeolite framework from $Ru(bpy)_3^{2+}$ to methyl viologen in ITQ-2 zeolite (formed by delamination of the precursor of MCM-22) was found to occur by time resolved spectroscopy [39].

In contrast to studies discussed above where electron transfer occurs within the zeolite, other studies have

investigated the electron transfer from the zeolite to species in solution. The oxidation of diphenylamine (DPA) and triphenylphosphine (TPP) in solution by photoexcitation of two sensitizers 9,10-dicyanoanthracene (DCA) and 9-cyanoanthracene (CA) in zeolite Y was studied [40]. Long-lived excited states of the zeolite-bound sensitizers (~ 100 ns) as compared to solution (13 ns) were observed. Electron transfer from the photoexcited sensitizers in the zeolite to DPA and TPP were observed only if Fe^{2+} was present in the zeolite. Using Fe^{2+} –DCA-zeolite Y and TPP in solution, photolysis resulted in formation of the phosphine oxide $P(C_6H_5)_3O$ in aerated solution. In the presence of AgF, TPP was converted to $(C_6H_5)_3CF$ and TPP to $P(C_6H_5)_3F_2$. It was proposed that TPP and DPA radical cations were formed as intermediates via electron donation to the zeolite-bound sensitizers DCA and CA mediated through the Fe^{2+} [40].

Electron transfer from photoexcited $Ru(bpy)_3^{2+}$ in K^+ -exchanged zeolite to a bipyridinium salt *N*-[3-(dicyclohexylmethyl)oxypropyl]-*N'*-methyl-4,4'-bipyridinium, $DCHMV^{2+}$ in solution showed increasing yields of the radical cation $DCHMV^+$ if crown ethers that bound K^+ more strongly were added to the solution [41]. This observation was interpreted as indication of injection of K^+ ions from zeolite into solution along with electron transfer from the $Ru(bpy)_3^{2+}$ to the bipyridinium in solution, schematically presented in Fig. 2. With crown ethers that binds potassium ion more strongly, the back electron transfer from the bipyridinium radical cation to the $Ru(bpy)_3^{3+}$ in the zeolite was slowed down. There were two other interesting features of this study, no $Ru(bpy)_3^{3+}$ was detected and the yield of the bipyridinium radical cation was 50 times as much as the $Ru(bpy)_3^{2+}$ on the surface of the zeolite. It was proposed that the zeolite framework was acting as the electron donor to the $Ru(bpy)_3^{3+}$.

A fundamental study of the influence of the rotational mobility of the donor $Ru(bpy)_3^{2+}$ on electron transfer to methylviologen inside the zeolite was carried out [42]. $Ru(bpy)_3^{2+}$ was synthesized in zeolite Y with diameter of 13 Å, and in EMT, with hypercage dimensions of 13×14 Å. Using solid state 2H NMR spectroscopy, significant motion of $Ru(bpy)_3^{2+}$ in EMT was

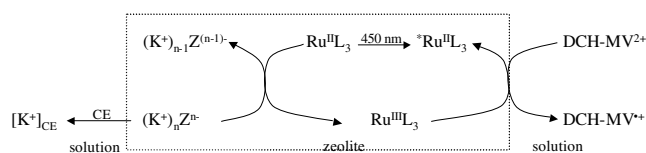


Fig. 2. Schematic diagram of electron transfer from intrazeolitic $Ru(bpy)_3^{2+}$ to the bipyridinium ion $DCH-MV^{2+}$ in solution along with the simultaneous liberation of K^+ from the zeolite to solution and complexation of the cation by crown ether. The zeolite is proposed as the source of electron for reducing $Ru(bpy)_3^{3+}$ (reprinted from Ref. [41]).

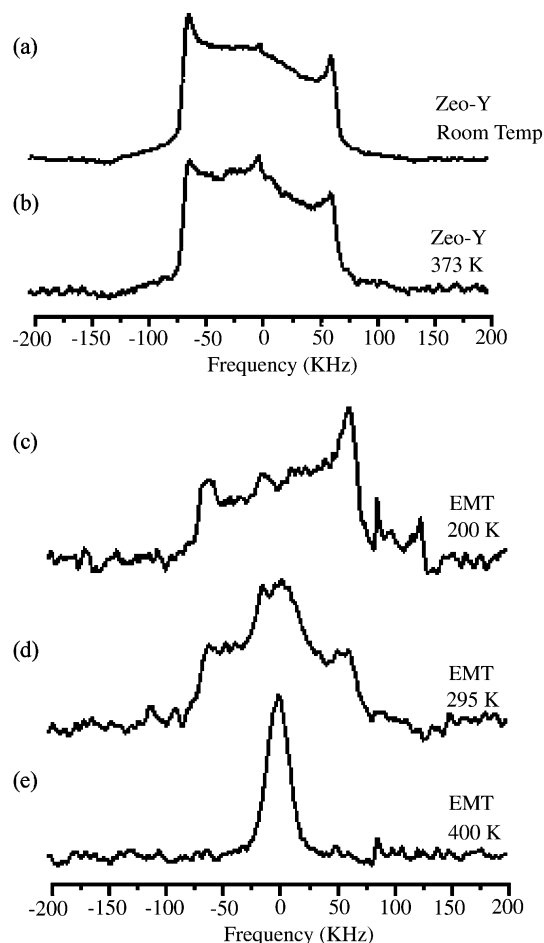


Fig. 3. Temperature-dependent ^2H quad-echo solid-state NMR spectra of (a,b) $\text{Ru}(\text{bpy})_3^{2+}$ in zeolite Y at room temperature and 373 K (c–e) and $\text{Ru}(\text{bpy})_3^{2+}$ in zeolite EMT at 200, 295 and 400 K all with deuterated bipyridine ligands (reprinted from Ref. [*42]).

noted even under ambient conditions, whereas in zeolite Y, the molecule was frozen at temperatures upto 100 °C, as evident from the Pake powder patterns of Fig. 3. The photoelectron transfer from the excited $\text{Ru}(\text{bpy})_3^{2+}$ to methyl viologen and the back electron transfer was faster in EMT as compared to zeolite Y, demonstrating that the geometrical arrangement of donor and acceptor influences the electron transfer dynamics.

4. Photooxygenation reactions within zeolite

There continue to be reports on exploiting the intracrystalline zeolite environment to activate organic molecules to promote oxidation reactions with molecular oxygen (O_2). It was shown that perfluorohexane solvents are better at transferring molecules with high fluorophobicity into the zeolite cages over hexane and stabilizing reactive singlet oxygen, potentially extending the synthetic potential of intrazeolite photooxidation for organic molecules [*43].

Photooxygenation of 1-butene in zeolite Y and led to a mixture of saturated and unsaturated carbonyl compounds. The electrostatic fields due to the cations were important in establishing the product ratios [44]. It was pointed out that recovery of the products from the zeolite was difficult.

The oxidation of cyclohexane and cyclohexene in Ba–Y was studied using both molecular oxygen and photochemically produced tert-butyl hydroperoxide (TBHP). Cyclohexane was photooxidized with oxygen to form cyclohexanone (80%) and did not react with TBHP. Photooxidation of cyclohexene with O_2 produced 2-cyclohexene-1-one as the major product (35%), whereas the dark reaction with TBHP produced 1,2-epoxycyclohexane (46%) [45].

Photooxygenation of aromatic alkenes such as styrene, 1,1-diphenylethene, *cis*- and *trans*-stilbenes and triphenylethene were studied. Charge transfer absorption bands were observed for styrene and stilbenes. The major products in all four oxidation reactions were benzaldehyde and benzophenone. It was suggested that the electrostatic fields stabilized the alkene cation radicals and O_2^- , the reactive intermediates [*46].

Comparison of photooxygenations of organic sulfides in zeolites and solutions have shown that the zeolite environment enhances the rates of reactions, suppresses the cleavage reaction (Pummerer rearrangement), and alters the sulfoxide-sulfone ratio. The role of the cation interaction with the intermediate persulfoxide was proposed to be important in influencing the oxidation [47].

5. Zeolite composites

Several studies have appeared recently on synthetic photochemistry using zeolite-titanium dioxide (TiO_2) composites. Intermolecular cyclization reaction of ethanol and ethylenediamine on TiO_2 /zeolite (zeolites Y, H-ZSM-5, H-beta) led to *trans*-1,4,6,9 tetraazabicyclo [4.4.0] decane with yields upto 35% using visible light illumination for 15 h [*48]. TiO_2 -zeolite composite also promoted the formation of 2 methylquinoxaline and quinoxaline from *o*-phenylenediamine and propylene glycol in the presence of molecular oxygen and light [49]. Using a composite of H-zeolite beta and TiO_2 (5 wt%), piperazine (yield of 59%) was synthesized from *N*-(2,3-dihydroxypropyl)ethylenediamine [50].

Photoelectron transfer between zeolite encapsulated 2,4,6-triphenylpyrylium (TP^+) or $\text{Ru}(\text{bpy})_3^{2+}$ to nanometer sized TiO_2 clusters in the supercages have been studied. Proximity to the TiO_2 clusters results in quenching of the emission. Diffuse reflectance studies show the formation of $\text{Ru}(\text{bpy})_3^{3+}$ or pyranil radical, indicating that the TiO_2 can act as both donor (to excited TP^+) and acceptor (from photoexcited $\text{Ru}(\text{bpy})_3^{2+}$). Reactive oxygen species produced via the TiO_2 lead to horseradish peroxidase deactivation [*51].

$\text{Ru}(\text{bpy})_3^{2+}$ and TiO_2 incorporated into zeolite Y have been used in the oxidation of 2,4-dimethylaniline (2,4-xylydine) to dimethylphenols in the presence of H_2O_2 . The $\text{Ru}(\text{bpy})_3^{2+}$ was proposed to donate electrons into the conduction band of TiO_2 which then reacted with H_2O_2 to form hydroxyl radicals, the ultimate oxidizing agent. $\text{Ru}(\text{bpy})_3^{3+}$ which was formed as a result of the electron transfer also took part in the oxidation to make oxalic acid and other products [*52].

6. Photoenvironmental effects

There has been growing interest in the use of zeolite-based systems for photochemical degradation reactions. Fenvalerate upon UV photolysis in solution converts via a rapid decarboxylation reaction to form 2,3-diarylisohexanitrile [53]. With 2,4,6-triphenyl pyrylium (TP)-zeolite Y, decarboxylation followed by oxidative mineralization (38%) was observed using visible light (>350 nm). It was proposed that the TP-Y-photocatalyzed reaction occurred through the formation of fenvalerate radical cation.

Iron (Fe^{2+})-zeolite X showed significantly higher Fenton reactivity (through hydroxyl radicals) for phenol degradation as compared to Fe^{2+} on silica gel or alumina. The Fenton activity of the Fe^{2+} -zeolite was comparable to homogeneous Fenton chemistry [54]. In another study, degradation of 4-chlorophenol to phenol, hydroquinone, and maleic acid by hydroxyl radicals was observed using thiophene oligomers in Fe^{3+} -ZSM-5 as photocatalyst [*55]. Another photooxygenation catalyst involving $\text{Fe}(\text{bpy})_3^{2+}$ supported on Na-Y oxidized dyes such as malachite green to primarily benzophenone derivatives by dissolved O_2 [56].

Polyoxometalate ions supported on zeolites have been examined for photochemical degradation. Heteropolytungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) encapsulated inside titanium exchanged H-Y was found to provide a 20-fold increase in the photochemical reduction of methyl orange as compared to zeolite without the titanium species [57]. In another study, polyoxometalate salts $\text{H}_2\text{NaPW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ on zeolite Y were used to study UV-photodegradation of 1,2-dichlorobenzene in water. Degradation was four to eight times higher than with the polyoxymetalate alone and attributed to better contact of the organic and metalate, high oxygen binding and suppressed back-electron transfer reactions. These studies were done at pH of 1.0 and it is unclear if the zeolite maintained its structure or was just being used as a support [58].

Silver exchanged zeolite Y (2.42 wt% Ag) was found to induce a 80-fold increase in photodecomposition rates of carbaryl (1-naphthyl,*N*-methylcarbamate) as compared to solution. Formation of excimers between the organic and metal cluster was proposed to promote the

photodegradation. Addition of Suwannee River natural organic matter, which typically inactivates photocatalysts had no effect on the silver zeolite system [*59].

$\text{Fe}(\text{bpy})_3^{2+}$ -zeolite Y co-doped with TiO_2 (both interior and exterior of the zeolite) upon illumination was found to be an effective generator of reactive oxygen species from H_2O_2 for oxidation of the model pollutant 2,4-dimethylaniline [*60].

Films of zeolite powder and TiO_2 have been investigated for photochemical degradation. For gas phase degradation of benzene, humidity increased the degradation and photoactivity increased with aluminous zeolites [*61]. Sheets of zeolite Y/ TiO_2 (incorporated into paper pulp) prepared by a paper-making technique were effective in the UV-photodegradation of acetaldehyde, and toluene and formaldehyde, common constituents of indoor pollution [62,63]. These composite sheets are potentially applicable for walls and ceilings of indoor structures.

7. New photochemical materials based on zeolites

Para-phenylene oligomers of three to five phenylene rings have been synthesized in palladium containing basic zeolites by homocoupling of 1,4-phenylenediboric acid. These oligomers emit blue light upon excitation and result in long-lived excited states [64]. A study aimed at making light emitting materials used europium (Eu^{3+}) complexes with (1-(2-thenyl)-4,4,4-trifluorobutane-1,3-dione) within zeolite X. These compounds emit red light upon excitation in the near ultraviolet [*65].

ETS-10, a framework with linear Ti–O–Ti–O– chains in its defect-free state catalyzes the photopolymerization of ethene and, in the presence of oxygen, the partial oxidation to acetic acid and acetaldehyde. However, if the material is defective, then complete oxidation of ethene to carbon dioxide and water is observed in the presence of oxygen. The defects are associated with exposed titanium sites in the ETS-10 structure [*66].

Optical fibers coated with zeolites have been used for asymmetric photochemical reactions, photoisomerization and monitoring of emission of polyaromatic compounds [67]. Because of the coating of the zeolite on the fiber, uniform illumination can be achieved.

An example of sensing dissolved oxygen involves $\text{Ru}(\text{bpy})_3^{2+}$ in zeolite Y. Previous studies have noted that the quenching of photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ by oxygen can be used for sensing purposes. Compared to other supports, the advantage of zeolite is that the encapsulated $\text{Ru}(\text{bpy})_3^{2+}$ cannot be leached out. However, $\text{Ru}(\text{bpy})_3^{2+}$ in aluminous zeolite will not quench dissolved oxygen because of lack of transport of O_2 from water into the zeolite [*68]. However, with highly siliceous zeolites, transport of O_2 from water into the zeolite cages is

promoted and quenches $\text{Ru}(\text{bpy})_3^{2+}$, leading to a dissolved O_2 sensor [69].

8. Multifunctional zeolite based assemblies

In this section, we focus on using zeolites for making complex assemblies, in particular, artificial photosynthetic systems. Chlorophyll *a* was found to be stabilized on mesoporous silica and in the presence of methyl viologen, sacrificial electron donor (mercaptoethanol) and Pt catalyst led to H_2 formation upon visible light irradiation. This assembly has been referred to as a model for living leaf [70].

In natural photosynthesis, the membrane plays a key role in keeping the oxidative and reductive part of the photochemical chains separated. Zeolite membranes are being examined for artificial photosynthesis. Pinhole free zeolite membranes were made by spin coating nanocrystalline zeolite Y on alumina and blocking the pinholes with a positive photoresist, and shown in Fig. 4a. Charge transport across the membrane using $\text{Ru}(\text{bpy})_3^{2+}$ and EDTA on one side of the membrane, methyl viologen inside the zeolite, and propylviologen sulfonate on the other side of the membrane was demonstrated according to the scheme shown in Fig. 4b [71].

Employing the strategy of quaternization of the 2,2′N atoms of the conjugated bipyridine ligand, 1,4-bis[2-(4′-methyl-2,2′-bipyrid-4-yl)ethenyl] benzene, a polypyridyl complex of ruthenium (II) was tethered on the surface of zeolite Y (Fig. 5a). Visible light photolysis of the ruthenium-zeolite solid ion-exchanged with diquat (*N,N′*-tetramethyl-2,2′-bipyridinium) and suspended in a propylviologen sulfonate solution led to permanent formation of the blue propylviologen sulfonate radical ion in solution. The model that was proposed involved intrazeolitic charge transfer to intrazeolitic diquat followed by interfacial (zeolite to solution) electron transfer to propylviologen sulfonate in solution, as outlined in Fig. 5b [**72]. Tethering the Ru complex to the surface of the zeolite led to slower back electron transfer reaction, which made the electron transfer through the zeolite possible.

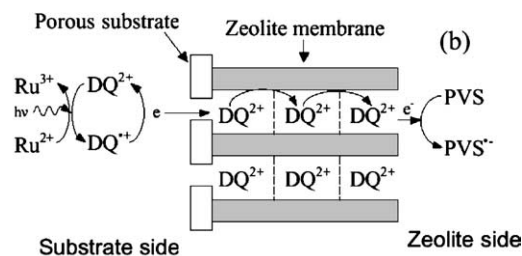
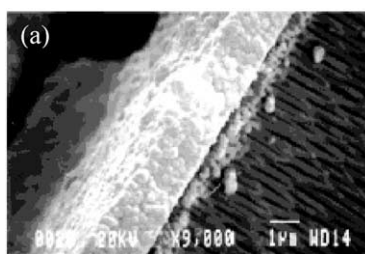


Fig. 4. (a) SEM micrograph of photoresist-coated zeolite membrane side view and (b) schematic representation of charge transport through a zeolite Y membrane (reprinted from Ref. [71]).

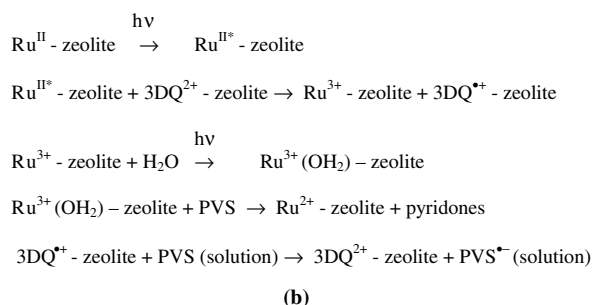
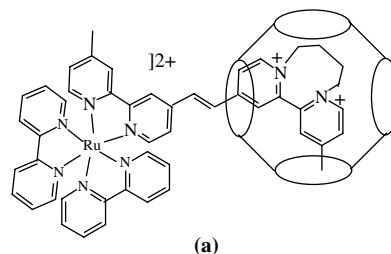


Fig. 5. (a) Tethered Ru(II) complex on zeolite Y and (b) Scheme for permanent charge transfer from tethered complex to PVS in solution mediated through intrazeolitic diquat (reprinted from Ref. [**72]).

Another paper has reported on membranes that can withstand the synthesis conditions necessary for synthesizing complexes on a zeolite membrane. Membranes of zeolite Y formed by the secondary growth process were sufficiently rigid and could be manipulated at temperatures suitable for making tethered complexes [73]. However, in order to establish a complete artificial photosynthetic system, the Ru(III) that is generated on one side of the membrane needs to transform water to O_2 [74], and the viologen radical formed on the opposite side of the membrane needs to make H_2 from water. Ruthenium oxide generated on the zeolite via thermal decomposition of $\text{Ru}_3(\text{CO})_{12}$ was used for photochemical reduction of water to hydrogen [75]. The catalyst demonstrated long-term stability, in contrast to Pt.

By coupling the zeolite-based membrane artificial photosynthetic assembly with the photonic antenna system in zeolite L channels [**12,13], a complete artificial photosynthetic system can be assembled. Such a zeolite-based assembly will be one of the most detailed artificial mimic of the natural photosynthetic system.

9. Major recent advances

There continue to be major strides in the area of light-activated processes in zeolites. It is becoming increasingly clear that the zeolite framework is an active host. Besides confinement of molecules in a well-ordered manner, the zeolite cations have a profound effect on structure of the enclosed molecule and generate strong electrostatic fields that polarize molecules, thus altering their photoreactivity. The ordered topology of zeolites also allows for novel spatial arrangement of molecules allowing the design of complex supramolecular assemblies. Some of the important milestones over the past two years include

- role of the zeolite framework as an electron acceptor and donor,
- strong influence of extra-framework cations in photochemical reactions,
- novel ship-in-a-bottle syntheses of complex molecules in zeolites,
- photochemical reactions on zeolite-metal oxide composites,
- environmental remediation with zeolites,
- multifunctional photochemical assemblies within zeolites.

Acknowledgements

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- * of special interest;
** of outstanding interest.
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