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Photosensitized Oxidation of Alkenes Adsorbed on Pentasil Zeolites

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Abstract: Photosensitized oxidation of *trans,trans*-1,4-diphenyl-1,3-butadiene (DPB), *trans*-stilbene (TS), and 2,3-dihydro-γ-pyran (DHP) included in the internal framework of Na-ZSM-5 zeolites was investigated. The zeolite samples having adsorbed the alkenes were suspended in isooctane or pentaerythritol trimethyl ether (PTE), and the sensitizers, 9,10-dicyanoanthracene (DCA) and hypocrellin A (HA), were dissolved in the solution. The molecular sizes of both of the sensitizers and the solvents are greater compared with the channels of the zeolites. The isolation of the alkenes within the zeolites from the sensitizers in surrounding solution prevents them from undergoing electron transfer. On the other hand, singlet oxygen was produced in the solution and diffused into the internal framework of the zeolites to react with the alkenes. Thus, only singlet oxygen oxidation products were obtained and no product derived from superoxide radical anion was detected. By addition of water after the alkene adsorption, the photosensitized oxidation product distributions can be dramatically varied depending upon the aluminum content of the zeolite framework and the molecular dimensions of the substrates. Possible interpretations of these effects are discussed in terms of the locations of the reactants.

Introduction

Selectivity in organic phototransformations continues to be one of the main topics of current interest. Of the various approaches use of organized and constrained media has shown considerable promise.[1] Molecular sieve zeolites represent a novel and unique class of materials.[2] This material may be regarded as open structures of silica in which silicon has been substituted by aluminum in a well-defined fraction of the tetrahedral sites. The frameworks thus obtained contain pores, channels, and cages of different dimensions and shapes. The pores and cages can accommodate, selectively according to size/shape, a variety of organic molecules of photochemical interest, and provide restrictions on the motions of the included guest molecules and reaction intermediates. For example, the internal surface of ZSM-5, a member of the pentasil family, consists of two types of pore systems (channels):[3] one is sinusoidal with a near circular cross section of ca. 5.5 Å, and the other is straight and perpendicular to the sinusoidal channels. The straight channels are roughly elliptical with dimensions of ca. 5.2 × 5.8 Å. These channels of ZSM-5 can allow the adsorption of benzene and other molecules of similar molecular size, but prevent molecules which possess a larger size/shape from being sorbed into the internal framework.[1a,1b]

The dye-sensitized photooxidation of alkenes has been extensively investigated. There are two well-established types of such photooxidation: energy transfer pathway and electron transfer pathway.[4] The energy transfer pathway involves energy transfer from the triplet sensitizer to the ground-state oxygen to generate singlet oxygen, then the generated singlet oxygen reacts with the substrate.[5] For example, Diels−Alder reaction of conjugated dienes, “ene” reaction of olefins with allylic hydrogen, and dioxetane reaction of olefins that do not feature an allylic hydrogen belong to this type. In electron transfer photosensitized oxidation electron-deficient sensitizers are generally used.[6] Electron transfer from alkene to the sensitizer in its excited states results in alkene radical cation and sensitizer radical anion, which subsequently reduces O_2 to give superoxide radical anion. The generated superoxide radical anion reacts with the alkene radical cation to yield the oxidation products. In many cases, the two types of photooxidation occur simultaneously, and the selectivity of the oxidation reactions is low. To gain the selectivity, the photosensitized oxidation of alkenes included within zeolites has been investigated.[7−9] Fox and coworkers used $Ru(bpy)_3^{2+}$ exchanged into zeolite Y as the sensitizer to oxidize tetramethylethylene and 1-methylcyclo-

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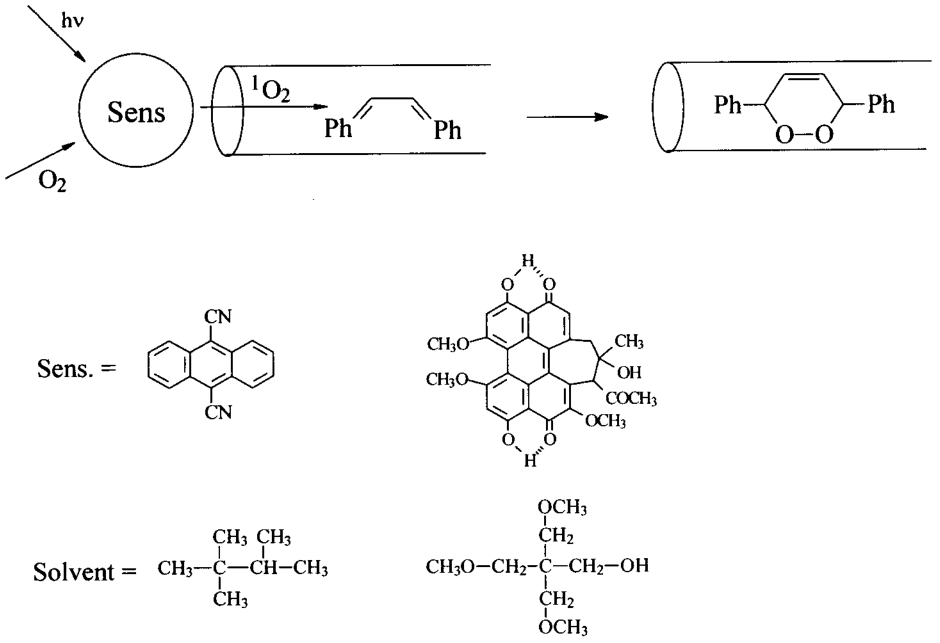
Scheme 1



hexene.[7] The photolysis was performed in $Ru(bpy)_3^{2+}$-exchanged zeolite slurry in methanol containing the alkene. They found that the photogenerated singlet oxygen within zeolites cages freely diffuses to solution where it reacts with the alkene with normal selectivity. Recently, Frei and co-workers stabilized the olefin•O_2 charge-transfer (CT) complex by enclosing the reactants in the cages of zeolite NaY.[8a–c] Irradiation of the complex at its long wavelength absorption band resulted in oxidation of the alkene. They have extended their study to toluene•O_2 and cyclohexane•O_2 complexes in alkali and alkaline-earth exchanged zeolite Y and applied this method to selective oxidation of a tertiary alkane C−H group.[8d–g] More recently, Ramamurthy and co-workers studied the oxidation of *trans*-stilbene and *trans*-4,4′-dimethoxystilbene included in X and Y zeolites.[9a] The zeolite having adsorbed both the alkene and the sensitizer was photolyzed in hexane slurry under oxygen atmosphere. They found that the oxidation was initiated via an electron transfer pathway, which is contrasted with that in homogeneous solution (energy transfer pathway). On the other hand, in the studies of the oxidation of a series of olefins included within dye-exchanged X and Y zeolites, they could generate singlet oxygen within the zeolite by irradiating the dye and direct the reactive oxygen toward a particular face of the olefin, thus obtaining a high selectivity in the products of the oxidation.[9b–e] Furthermore, photosensitization reactions of olefin in pentasils have also been established.[10] In the above examples, the sensitizer and the substrate were localized and confined within the restricted space of a zeolite, and closely interacted with each other. In the present work, we study the photosensitized oxidation of alkenes on zeolites. *trans,trans*-1,4-Diphenyl-1,3-butadiene (DPB), *trans*-stilbene (TS), and 2,3-dihydro-γ-pyran (DHP) were selected as the alkenes, and 9,10-dicyanoanthracene (DCA) and hypocrellin A (HA) were the sensitizers. We trap the alkenes in the channels of ZSM-5 zeolites and isolate the photosensitizers in the surrounding solution (Scheme 1). The isolation of the substrate within the zeolite from the sensitizer in the solution outside inhibits the electron transfer. On the other hand, singlet oxygen still can be generated in the solution, and is able to diffuse into the ZSM-5 channel to react with the alkene. Thus, we observed that the photosensitized oxidation proceeds with a high degree of selectivity, which is not observed in the solution photooxygenation.

Result and Discussion

General. We used the ZSM-5 zeolites with a different Si/Al ratio as the reactive media: a “low” Al content (Si/Al = 55) and a “high” Al content (Si/Al = 25). All the zeolites were sodium cation exchanged forms. Inclusion of DPB, TS, and DHP within the zeolites was achieved by using cyclohexane as the solvent. The powder of ZSM-5 having adsorbed the substrate was collected by filtration of the solvent and dried under nitrogen, then washed with isooctane to remove the substrate adsorbed on the external surface of ZSM-5. The loading level was kept at ca. 50 mg of substrate on 1 g of ZSM-5. The sample prepared above was suspended in isooctane or pentaerythritol trimethyl ether (PTE).[11] The sensitizers, DCA or HA, were dissolved in the solution. The choice of the solvents and sensitizers was motivated by the desire that they were prevented from being sorbed into the ZSM-5 channel due to their size and shape characteristics.[12] Thus, the internal framework of ZSM-5 is “dry”, and the substrate is protected from being extracted to the solution during photolysis.

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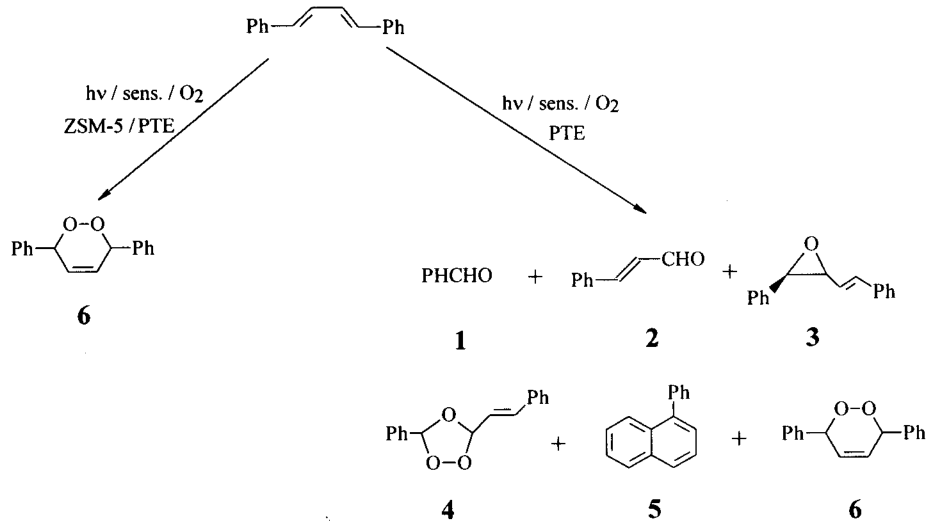
(12) The kinetic diameter of isooctane is >6.2 Å based on the fact that for neopentane the kinetic diameter is 6.2 Å. Thus, it cannot be sorbed into the ZSM-5 internal framework, see: Turro, N. J.; Wan, P. *J. Am. Chem. Soc.* **1985**, *107*, 678. PTE has a greater kinetic diameter compared with isooctane.

Scheme 2



The solution was saturated with oxygen by bubbling the gas during photolysis. Generally, after 4 h of photolysis the conversion of the starting material was near 100%. Similar conversion was obtained in PTE in the absence of ZSM-5 zeolite after about 1 h of irradiation. After photolysis, the ZSM-5 powder was separated from the solvent by filtration. The products were extracted with dichloromethane and analyzed by gas chromatography. Material balance in general was greater than 90%.

Oxidation of *trans,trans*-1,4-Diphenyl-1,3-butadiene (DPB). Irradiation of oxygen-saturated DPB solution in PTE containing DCA or HA with visible light gave benzaldehyde **1**, cinnamaladhyde **2**, epoxide **3**, ozonide **4**, and endoperoxide **6** (Scheme 2). In addition, a small amount of 1-phenylnaphthalene **5** was detected. All the products were isolated by column chromatography and identified by their spectral properties and by comparison with authentic samples. The product distribution is slightly dependent on the sensitizers and is shown in Table 1. In all cases, the main products are **1** and **2**. It has been established that DCA[6] and HA[13] can act both as singlet oxygen sensitizer and electron transfer sensitizer. Obviously, **6** is a product of 1,4-cycloaddition of singlet oxygen ($^1O_2$) to DPB. The other products are presumably derived via the electron-transfer pathway.[14] As Foote suggested for the DCA-sensitized oxidation of stilbene,[6c] **1** and **2** are most likely derived from an intermediate dioxetane, a cycloaddition product of DPB$^+$, and superoxide anion (O_2^-), which would decompose under reaction conditions. **3** could be formed by the Bartlett reaction.[6c,14] **4** is possibly a secondary photooxygenation product from **3**. Formation of **5** is probably due to cationic rearrangement of DPB.

In contrast, the DCA- and HA-sensitized photooxidation of DPB adsorbed on the internal surface of ZSM-5 zeolites gave **6** as the unique product (Table 1 and Scheme 2). The yield of this product was 100% based on the consumption of the starting material. The Al content in the zeolites (Si/Al = 55 or 25) showed no effect on the oxidation product distribution. Control experiments showed that for oxidation to occur, both the sensitizer and light are required. Evidently, the isolation of DPB within the zeolite channels from the sensitizer in the solution outside prevents them from undergoing electron transfer. Thus, no photooxidation products derived from the electron transfer pathway were detected. This proposal was confirmed by the fact that while the fluorescence of DCA and HA in PTE solution was apparently quenched by DPB according to an electron transfer mechanism, the fluorescence quenching was not observed at all when DPB was included into ZSM-5 zeolite and DCA or HA was dissolved in PTE. On the other hand, $^1O_2$ can be formed in the solution by energy transfer from the triplet-state sensitizer to the ground-state oxygen. The species $^1O_2$ is small and uncharged and has a relatively long lifetime and properties which allow it to diffuse freely from the surrounding solution to the internal framework of ZSM-5 zeolite. 1,4-Cycloadditon of $^1O_2$ to DPB in the internal surface of ZSM-5 results in endoperoxide **6**.

Table 1. Product Distributions for Photosensitized Oxidation of DPB in Homogeneous Solution and on the Internal Surface of ZSM-5 Zeolites, and Effects of Coadsorbed Water on the Product Distributions

		product yield,[a] %					
sens.	reaction medium	1	2	3	4	5	6
DCA	PTE	73	73	16	4	4	3
DCA	dry ZSM-5 (Si/Al = 55)-PTE[b]	0	0	0	0	0	100
DCA	dry ZSM-5 (Si/Al = 25)-PTE[b]	0	0	0	0	0	100
HA	PTE	53	53	16	4	14	13
HA	dry ZSM-5 (Si/Al = 55)-PTE[b]	0	0	0	0	0	100
HA	dry ZSM-5 (Si/Al = 25)-PTE[b]	0	0	0	0	0	100
DCA	wet ZSM-5 (Si/Al = 55)-PTE[c]	0	0	0	0	0	100
DCA	wet ZSM-5 (Si/Al = 25)-PTE[d]	17	17	21	9	50	3
HA	wet ZSM-5 (Si/Al = 55)-PTE[c]	0	0	0	0	0	100
HA	wet ZSM-5 (Si/A = 25)-PTE[d]	23	23	25	7	40	5

[a] Estimated error limits were 2%. [b] Dry sample was suspended in PTE. [c] Wet sample with water uptake of 9% (w/w) was suspended in PTE. [d] Wet sample with water uptake of 10% (w/w) was suspended in PTE.

Ramamurthy and co-workers reported that inclusion of α,ω-diphenyl polyenes in thermally activated ZSM-5 zeolite leads

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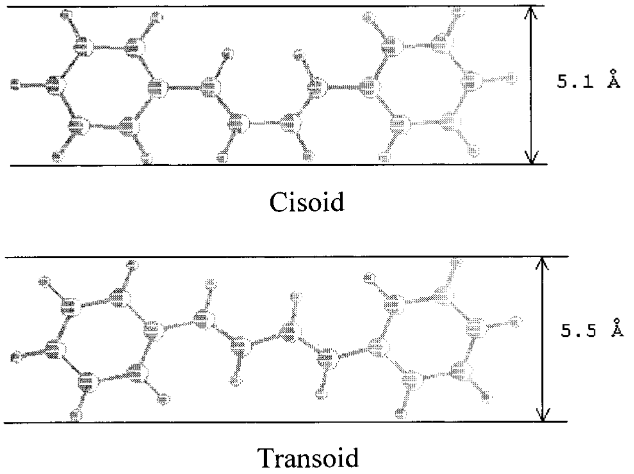

Figure 1. Geometries of DPB conformers optimized by AM1 calculations.

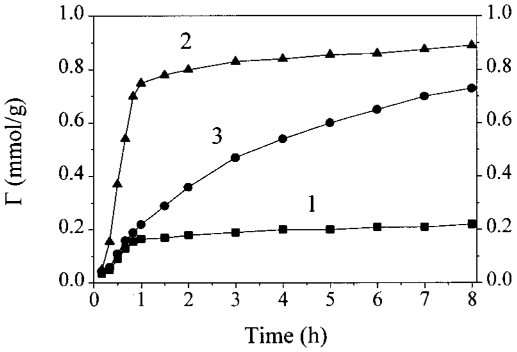

Figure 2. Amounts of *o*-xylene (curve 1), *p*-xylene (curve 2), and DPB (curve 3) adsorbed into ZSM-5 zeolites as a function of soaking time of the zeolite in the substrate solutions in cyclohexane. The experiment was performed by using 20 mg of substrate dissolved in 30 mL of cyclohexane and exposed to 100 mg of zeolite with vigorous stirring.

to the rapid formation of cation radicals of the polyenes.[1b,15] These cation radicals are stabilized within the zeolite host and can be conveniently studied by conventional spectroscopic techniques. Indeed, we noticed that the initially white NaZSM-5 zeolite became pale-pink when DPB was included. Thus, we believe that DBP cation radicals were formed. Since the amount of the cation radicals is small (about 0.1% of the total loading capacity of the zeolite),[15] it is expected that the formation of the cation radicals does not significantly affect the photosensitized oxidation of DPB.

It is worth noting that *trans,trans*-1,4-diphenyl-1,3-butadiene in solution exists in two conformational isomers: cisoid and transoid.[14,16] At equilibrium the main conformer is the transoid (ca. 99%), and the cisoid is presented only in ca. 1%. The 1,4-cycloaddition of singlet oxygen to 1,3-diene to form endoperoxide is concerted and analogous to the Diels−Alder reaction. This reaction requires a six-membered ring transition state. Only the cisoid conformer can satisfy such a requirement, and in order to undergo 1,4-cycloadditon with singlet oxygen the transoid first has to be isomerized to the cisoid. Due to the kinetic equilibrium between the two conformers in solution, the cycloaddition can proceed until all the diene is converted to the products. On the other hand, it has been established[16] that on silica surface the conformational change is restricted and the DCA-sensitized oxidation of DPB in this medium could not result in formation of **6.** To our surprise, in the internal surface of ZSM-5, **6** is quantitatively produced in the photosensitized oxidation of DPB and the conversion of the reaction can reach 100%. This observation is proposed to result from the differences in size and shape of the two conformers, thus showing different adsorption behavior on ZSM-5 zeolite. We used the semiempirical method AM1 program to calculate the energies of the various conformations of DPB. The geometries having the lowest energies are the cisoid and transoid conformers, and are shown in Figure 1. The molecular width of the cisoid is calculated to be ca. 5.1 Å, while that for the transoid is ca. 5.5 Å. Thus, the transoid possesses a shape and size which are relatively large (bulky) to fit into the channels of ZSM-5, while the cisoid could readily enter and be accommodated into the channels of ZSM-5. The transoid conformer in solution could be first isomerized into the cisoid one, and then enter into the ZSM-5 channels. As a result, all DPB molecules adsorbed in the channels of ZSM-5 exist in the cisoid conformer. Such remarkable size and shape selectivity displayed by ZSM-5 is not unprecedented.[10,17] For example, *trans*-stilbene can be readily incorporated within the channel systems of this zeolite, while by contrast the different dimension precludes *cis*-stilbene to penetrate inside the internal voids of the zeolite.[10,17]

To support the above proposal, we have carried out adsorption studies of DPB on ZSM-5 and compared them with those of *p*-xylene and *o*-xylene. It has been established[18] that *p*-xylene can diffuse into and be adsorbed within the internal surface of ZSM-5, while the ortho isomer, *o*-xylene, possesses a size and shape that inhibits diffusion into the ZSM-5 channel system. We prepared solutions of the above three compounds in cyclohexane. To each solution a preweighted amount of ZSM-5 zeolite was added and vigorously stirred at room temperature for a certain time. After filtering, the filtrate was analyzed for unadsorbed substrate by GPC. In this way, the amount of substrate adsorbed from solution was calculated. We measured the adsorbed amount of substrate as a function of soaking time of the zeolite in the substrate solution, and the results are shown in Figure 2. The adsorptions for *p*-xylene, which can diffuse into ZSM-5 channels, and *o*-xylene, which cannot enter the channels, reach equilibrium within 15 min, while the amount of adsorbed DPB gradually increases with adsorption time within 8 h. Evidently, this significant difference in adsorption rate between DPB and the xylene isomers is ascribed to the fact that the cisoid conformer of DPB, which is able to diffuse into ZSM-5 channels, exists in low concentration in solution. Thus, the adsorbed rate of DPB is smaller compared with *p*-xylene. As the cisoid conformer is adsorbed into ZSM-5 channels, the transoid in solution is isomerized into the cisoid. The transoid can be visualized as a reservoir of the cisoid. Eventually, a large amount of DPB is adsorbed into ZSM-5.

Oxidation of *trans*-Stilbene (TS). As observed in the case of DPB, the photooxygenation of TS sensitized by DCA or HA differed significantly when included in ZSM-5 zeolite compared to that in homogeneous solution. The oxidation products in homogeneous solution are remarkably dependent on the sensitizers and conditions used. Foote reported previously[6c] that in acetonitrile with DCA as the sensitizer, the oxidation products were benzaldehyde (**1**), *cis*-stilbene (**7**), *trans*-2,3-diphenylox-

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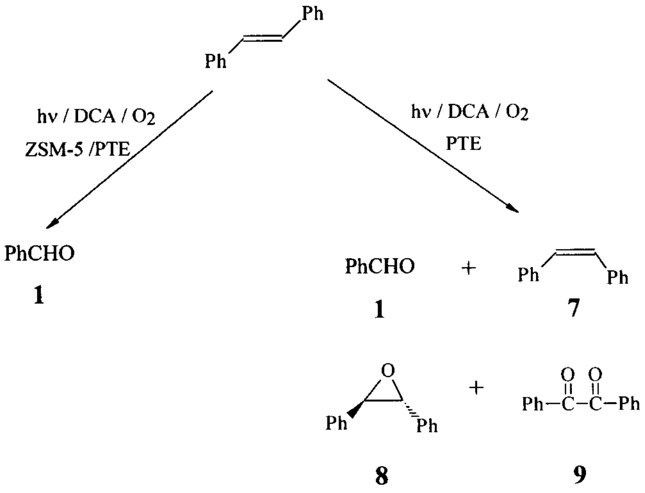
Scheme 3



Scheme 4

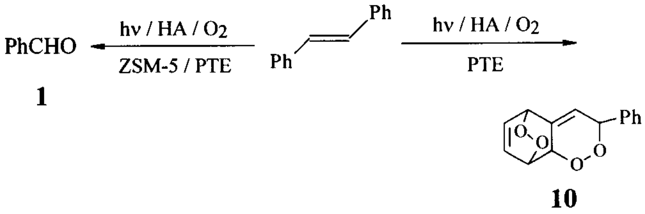
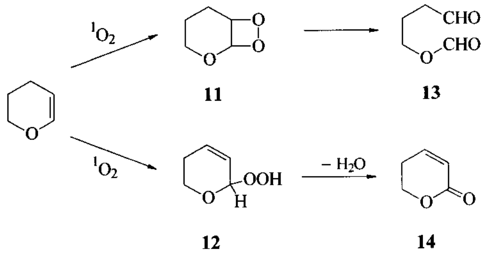


Table 2. Product Distributions for Photosensitized Oxidation of TS in Homogeneous Solution and on the Internal Surface of ZSM-5 Zeolites, and Effects of Coadsorbed Water on the Product Distributions

		product yield,[a] %				
sens.	reaction medium	1	7	8	9	10
DCA	PTE	48	12	28	12	0
DCA	dry ZSM-5 (Si/Al = 55)-PTE[b]	100	0	0	0	0
DCA	dry ZSM-5 (Si/Al = 25)-PTE[b]	100	0	0	0	0
HA	PTE	3	0	0	0	97
HA	dry ZSM-5 (Si/Al = 55)-PTE[b]	100	0	0	0	0
HA	dry ZSM-5 (Si/Al = 25)-PTE[b]	100	0	0	0	0
DCA	wet ZSM-5 (Si/Al = 55)-PTE[c]	100	0	0	0	0
DCA	wet ZSM-5 (Si/Al = 25)-PTE[d]	55	13	25	7	0
HA	wet ZSM-5 (Si/Al = 55)-PTE[c]	100	0	0	0	0
HA	wet ZSM-5 (Si/Al = 25)-PTE[d]	3	0	0	0	97

[a] Estimated error limits were 2%. [b] Dry sample was suspended in PTE. [c] Wet sample with water uptake of 9% (w/w) was suspended in PTE. [d] Wet sample with water uptake of 10% (w/w) was suspended in PTE.

Scheme 5



irane (**8**), and benzil (**9**) (Scheme 3). All these products were produced via the electron transfer pathway. However, Matsumoto reported[19] that at room temperature in CCl_4 with tetraphenylporphrin as the sensitizer, the photooxidation of TS gave diendoperoxide **10** (Scheme 4) in a yield of 16% based on the reacted starting material. The other major product, benzaldehyde, was produced in 80% yield. This reaction is proposed to proceed via the energy transfer pathway. We found that in PTE with DCA as the sensitizer, the photooxidation products are the same as those obtained in the DCA-sensitized reaction in acetonitrile (Scheme 3), but the product distribution is slightly changed (Table 2). On the other hand, in the same solvent with HA as the sensitizer, the main product is **10** (Scheme 4 and Table 2). When TS is included within ZSM-5 zeolite (Si/Al = 55 or 25) and the sensitizer is solublized in the surrounding solvent PTE, the photooxidation of TS sensitized by DCA or HA yields benzaldehyde as the unique product (Schemes 3 and 4 and Table 2). The mass balances of this reaction for the two sensitizers are all close to 100%. As in the case of DPB, the isolation of TS within the zeolite from the sensitizer in the solution outside prevents electron transfer between the substrate and the sensitizer to occur. Thus, no superoxide anion is expected to be produced. Obviously, benzaldehyde is derived via the energy transfer pathway. The singlet oxygen generated via energy transfer from the triplet sensitizer to the ground-state oxygen in solution diffuses into the internal framework of ZSM-5 and reacts with TS to form 3,4-diphenyl-1,2-dioxetane, which would decompose to yield benzaldehyde under reaction condition. We note that in the HA-sensitized photooxidation diendoperoxide **10** was not produced. This observation is contrary to the result of the reaction for TS with singlet oxygen in solution. The absence of **10** in the oxidation products within the zeolite is probably due to the constrained space within ZSM-5 channels which is not big enough to accommodate the molecule of **10**.

Oxidation of 2,3-Dihydro-γ-pyran (DHP). The photooxidation of DHP in homogeneous solutions has been extensively investigated.[20] Upon photosensitized oxidation DHP yields two primary products: a cycloaddition product, dioxetane **11**, and an "ene" reaction product, allylic hydroperoxide **12** (Scheme 5). The products actually isolated under normal preparative conditions are the derived aldehydroformate **13** and dihydropyrone **14**. The ratio of **13** to **14** is very dependent on the solvent polarity, with the polar solvents favoring the cycloaddition mode of reaction over the ene type. For example, this ratio varies over a 59-fold range as the solvent is changed from benzene to acetonitrile. Since all of the above products are generated via the singlet oxygen pathway, we expect that both **13** and **14** could be produced in the photosensitized oxidation of DHP included in ZSM-5 zeolite, and the ratio of **13** to **14** would be decided by the character of the internal framework of ZSM-5.

In Table 3 are given the product distributions of the photooxidation of DHP sensitized by HA in homogeneous solutions and on the internal surface of ZSM-5 zeolites. The

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Table 3. The Ratio of **13** to **14** in Potosensitized Oxidation of DHB by HA in Homogeneous Solution and on the Internal Surface of ZSM-5 Zeolites

sample	ratio of **13** to **14**[a]
isooctane solution	10:90
PTE solution	58:42
dry ZSM-5 (Si/Al = 55)-isooctane[b]	40:60
dry ZSM-5 (Si/Al = 55)-PTE[c]	40:60
dry ZSM-5 (Si/Al = 25)-isooctane[b]	48:52
dry ZSM-5 (Si/Al = 25)-PTE[c]	48:52
wet ZSM-5 (Si/Al = 55)-isooctane[d]	83:17
wet ZSM-5 (Si/Al = 55)-PTE[e]	82:18
wet ZSM-5 (Si/Al = 25)-isooctane[f]	94:6
wet ZSM-5 (Si/Al = 25)-PTE[g]	94:6

[a] Estimated error limits were 2%. [b] Dry sample was suspended in isooctane. [c] Dry sample was suspended in PTE. [d] Wet sample with water uptake of 9% (w/w) was suspended in isooctane. [e] Wet sample with water uptake of 9% (w/w) was suspended in PTE. [f] Wet sample with water uptake of 10% (w/w) was suspended in isooctane. [g] Wet sample with water uptake of 10% (w/w) was suspended in PTE.

ratio of **13** to **14** changes from 10/90 in isooctane to 58/42 in PTE. However, when DHP is included in ZSM-5 zeolites, the ratio of **13** to **14** is greater than that seen in isooctane, but smaller than that in PTE. Of particular interest is that this ratio is independent of the solvents used, but dependent on the Al content of ZSM-5 zeolites with the high Al content favoring the formation of **13** over **14**. The solvent-independent ratio suggests that the oxidation reaction occurs within the internal framework of ZSM-5. Evidence has been presented that there exist hydrophilic centers in the internal surface of pentasils, the most common of which are hydroxyl groups or cations associated with a tetrahedrally coordinated aluminum, and the remaining regions in the internal surface are hydorphobic.[21] The ratio of **13** to **14** might reflect the location of DHP, on average, in the internal channel of ZSM-5 zeolite. It has been suggested that within a zeolite alkene molecules are adsorbed to the surface near Al atoms due to the interaction between the π-electron density of the substrate and the cation of the zeolite.[9e,21a,22] Based on the unit cell composition ($Na_xSi_{96-x}Al_xO_{192}$)[21b] of NaZSM-5 zeolite, the concentration of Al is calculated to be ca. 6.3×10^{-4} and 2.3×10^{-4} M per gram of zeolite with a Si/Al value of 25 and 55, respectively. The loading of DHP employed in the present study was ca. 6×10^{-4} M per gram of zeolite. Thus, for a high Al content sample nearly every DHP molecule may associate with a cation near an Al atom, while for a low Al sample a large fraction of DHP has to be located in the weaker binding hydrophobic regions within the framework. As a result, the ratio of **13** to **14** for a high Al content sample is larger than that for a low Al content sample. The micropolarity in the vicinity of the cations within the zeolite is certainly much higher than that in a PTE solvent cage. However, we note that the ratio of **13** to **14** even for a high Al sample is smaller than that in PTE. This observation suggests that many factors beside micropolarity, such as steric factors and orientation of the alkene molecules, might influence the ratio of **13** to **14**.

Effects of Coadsorbed Water on Product Distribution. To support the mechanistic interpretation of the selectivity in photosensitized oxidation of alkenes adsorbed on ZSM-5 zeolites, we studied the effect of added water on the product distributions. The photolysis experiments described above were repeated after samples were saturated by water vapor. Water vapor was added to the samples prepared by deposition of the substrate on dry zeolite from cyclohexane followed by evaporation of the solvent. For the "high" Al content (Si/Al = 25) samples, the maximum amount of coadsorbed water was ca. 10% (w/w), and for the "low" Al content (Si/Al = 55) ones, ca. 9% (w/w). The samples were suspended in isooctane or PTE containing sensitizer DCA or HA, and irradiated as described above. The resulting product distributions are listed in Tables 1, 2, and 3 for DPB, TS, and DHP, respectively. The following facts are apparent from the data in these tables: (1) The photosensitized oxidation of DPB and TS wet samples with Si/Al =55 gave **6** and **1** as unique products respectively as in the case of the dry samples. Thus, for the samples with "low" Al content (high Si/Al ratio) ZSM-5 zeolite, no effect of coadsorbed water on the product distributions was observed. (2) On the contrary, for the wet samples with Si/Al = 25, the photosensitized oxidation products of DPB and TS are significantly different from those for the dry samples. The addition of water causes the product distributions to be more like those obtained in homogeneous solution. For example, the products for DPB wet samples in PTE were mainly derived via the electron transfer pathway. Furthermore, the HA-sensitized oxidation of TS wet sample gave **10** as the main product as in the case of the oxidation in PTE solution. (3) For the wet samples irrespective of the Si/Al ratio, the photosensitized oxidation of DHP gave **13** and **14**, and the ratio of **13** to **14** was significantly greater than those for dry samples.

The influence of added water is readily understood by consideration of the character of ZSM-5 zeolite and the location of the adsorbed substrates in the wet samples. It has been established[21] that water molecules are adsorbed at or near the hydrophilic aluminum sites in the zeolite framework to form clusters whose size is constrained by the size and shape requirement and by the hydrophobic nature of the internal void space. The portion of the ZSM-5 internal framework that is not near the water clusters is hydrophobic. Evidently, there are fewer sites available for water adsorption in the case of Al-poor ZSM-5 than there are for Al-rich ZSM-5 zeolites. Thus, the length of the hydrophobic regions within the channels of the wet Al-poor samples is longer than that for the wet Al-rich samples. As mentioned above, the concentration of Al is ca. 6.3×10^{-4} and 2.3×10^{-4} M per gram of zeolite for the samples with Si/Al of 25 and 55, respectively. The loadings of DPB and TS employed in this study were ca. 2×10^{-4} M per gram of zeolite, while that of DHP was ca. 6×10^{-4} M per gram of zeolite (each ca. 50 mg on 1 g of zeolite). Thus, before water is added the alkene molecules are probably adsorbed in the internal framework near Al atoms[9e,21a,22] except in the case of a DHP−Al-poor sample, where a large fraction of DHP is located in the hydrophobic regions within the framework as discussed above. As water is added, the hydrophobic alkene molecules are displaced or repelled by the more strongly bound water molecules. Thus, water has the effect of displacing alkene molecules from near the Al atom in the internal surface to the external surface or to the hydrophobic regions within the internal framework. As suggested by Turro and co-workers[21a] for *p*-methylbenzyl benzyl ketone, which possesses a molecular size similar to those of DPB and TS, in the wet Al poor ZSM-5 zeolite (Si/Al = 55), the hydrophobic regions would be large enough for accommodating DPB or TS molecules. It is expected that water would displace DPB and TS toward the hydrophobic portions of the framework. These DPB and TS

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molecules are still located in the internal framework and isolated from the sensitizer in the solution outside, and electron transfer from the substrate to the excited state sensitizer is prevented. Therefore, only the products derived from the energy transfer pathway were produced (**6** from DPB and **1** from TS) as in the case of dry samples. As a result, the coadsorbed water shows no effect on the product distributions of the photosensitized oxidation of DPB and TS on Al-poor ZSM-5 zeolite. In contrast, for wet samples with a higher content of Al (Si/Al = 25), the length of the hydrophobic regions in the channels is expected to be shorter compared with the size of the DPB and TS molecules.[21a] Addition of water to the dry samples would repel DPB and TS from the internal framework to the external surface or to the solution. Thus, the substrate is located on the outside of zeolite channels, and the photosensitized oxidation reaction can proceed via both energy transfer and electron transfer pathways. For the photosensitized oxidation of DPB and the DCA-sensitized oxidation of TS, the products are mainly derived from the electron transfer pathway, and in HA-sensitized oxidation of TS diendoperoxide **10** is quantitatively produced as in the reaction in solution. However, close inspection of Table 1 suggests that in comparison with the homogeneous solution, the yields of aldehydes **1** and **2** are significantly decreased, and the yields of the cationic rearrangement product **5** are increased for the wet zeolite samples. The difference in product distribution suggests that for the wet Al-rich zeolite samples the reaction probably occurs on the external surface of the zeolite rather than in solution.

The effect of the amount of coadsorbed water on the product distributions for DPB and TS samples was investigated. For a low Al content sample (Si/Al = 55), water uptake up to 9% (w/w) always gave **6** and **1** as the unique product for DPB and TS, respectively, as in the case of the dry samples. On the other hand, for a high Al content sample (Si/Al = 25), increasing the amount of the sorbed water in the region of 0−8% (w/w) gradually caused the product distributions to be more like those obtained in homogeneous solution. After the water uptake reached 8% (w/w), further adsorption of water (up to 10%) resulted in no more change in the product distributions. This observation can be explained in terms of site saturation for water adsorption. It has been established that for pentasil materials the extent of water uptake is directly attributable to the aluminum sites in the channels or on the external surface.[21] The amount of water required for site saturation was estimated to be ca. 4.4% and 8% (w/w) for the zeolite with a Si/Al ratio of 55 and 25, respectively by assuming a coordination of 6 H_2O molecules to each cation in the framework.[21] We speculate that for a high Al content sample at site saturation (8%) all the substrate molecules are repelled by water from the channels to the external surface. Thus, after the sites are saturated, addition of excess water results in no more change in product distribution. By contrast for a low Al content sample at site saturation (4.4%) all the substrate molecules are blocked in the hydrophobic pockets of the framework. The water further adsorbed might be on the external surface or at the pore mouths, because the inside of the channel is hydrophobic.

In the case of photooxidation of DHP adsorbed on ZSM-5 zeolite, the hydrophobic portions of the internal channels of the wet samples both with low (Si/Al = 55) and high (Si/Al = 25) Al contents could probably accommodate the DHP molecule, because of its relatively small size. The oxidation reactions for the wet samples would occur in the internal framework as in the case of dry samples. Thus, the ratio of **13** to **14** is not dependent on the solvents used, but instead on the microenvironment of the internal framework of the zeolite. The large values of these ratios suggest that DHP molecules would be surrounded by water clusters in wet samples.

Conclusions

The product distributions of DCA- and HA-sensitized oxidation of DPB, TS, and DHP adsorbed within ZSM-5 zeolites are significantly different from those for homogeneous solutions. The isolation of the substrates in the zeolite from the sensitizers in solution outside inhibits electron transfer reaction. The singlet oxygen generated in the solution can diffuse into the internal framework of the zeolite framework and reacts with the substrates. Thus, only the singlet oxygen oxidation products were produced. In the photosensitized oxidation of DPB and TS included in ZSM-5 zeolite, endoperoxide **6** and benzaldehyde **1** are the unique products, respectively. In the case of DHP, the ratio of **13** to **14** is independent of the solvents used. Coadsorption of water significantly modifies the pathway of the sensitized oxidation in a manner that depends on the Al content of the zeolites and the molecular dimensions of the substrate. For the sample of substrate with relatively large molecular size such as DPB and TS in low Al content (Si/Al = 55) zeolite, coadsorbed water causes the substrate molecules to move toward the hydrophobic regions of the channels and the oxidation reactions occur in the internal framework, whereas in a high Al content (Si/Al = 25) sample water repels DPB and TS molecules to the external surface of the zeolites or to the solution, and products derived from both electron transfer and energy transfer pathways are obtained. For substrate with a small molecular size such as DHP, in both the high and low Al content samples the oxidation reaction takes place within the internal framework of the ZSM-5 zeolite. This work demonstrates that one can use zeolites as media to increase the selectivity in photochemical reactions.

Experiment Section

Materials and Instruments. Unless otherwise noted, materials were purchased from Aldrich Chemical Co. and were used without further purifications. Hypocrellin A was kindly donated by Professor J.-Y. An of the Institute of Photographic Chemistry, Chinese Academy of Sciences. Isooctane, cyclohexane, and dichloromethane were spectra-grade. Pentaerythritol trimethyl ether (PTE) was synthesized by the reaction of pentaerythritol with methyl iodide in the presence of NaOH. Na-ZSM-5 zeolites with Si/Al = 55 and 25 were obtained from Nankai University. All the zeolites were sodium exchanged forms, and were baked at 550 °C for 10 h prior to use. The ^{1}HNMR spectra were recorded at 100 MHz with a Varian FX-100 spectrometer. Mass spectra were run on a VG ZAB GC-MS spectrometer. Gas chromatography was performed on a Shimadzu-7A with a 3% OV-17 column.

General Photolysis Procedure. The zeolite samples were activated at 550 °C for at least 1 h prior to use. For a typical photolysis experiment, an activated sample was added to the substrate solution in cyclohexane and stirred at room temperature for 1 h. The zeolite sample having adsorbed the substrate was collected by filtration of the solvent, dried under nitrogen, and washed with isooctane to remove the substrate adsorbed on the external surface of the zeolite. For the preparation of the wet sample, a cell having been loaded with dry sample was connected to a vacuum line with a reservoir of water as the source of water vapor. The sample was subsequently suspended in PTE (or in isooctane) in a Pyrex photolysis cell. To the cell a known amount of the sensitizer (DCA or HA) solution in PTE (or isooctane) was added. Oxygen was bubbled through the solution during photolysis. A 450-W medium-press Hanovia Hg lamp was employed as the light source, and a glass filter was used to cut off the light with wavelength <400 nm. The filter thus ensured the absence of direct excitation of the alkene substrate. After irradiation, the zeolite was collected by filtration and soaked and stirred in dichloromethane overnight. Analysis of the filtrate solution was performed by GPC. For preparative samples, the products were isolated by column chromatography and identified by their spectral properties.

Adsorption Rate Measurements. For adsorption rate study, to a preweighted amount of DPB, *p*-xylene or *o*-xylene (each ca. 20 mg) dissolved in 30 mL of cyclohexane was added 100 mg of zeolite and the mixture was then stirred vigorously at room temperature. The slurry was then filtered, and the filtrate was analyzed for substrate content by GPC. The amount of the substrate adsorbed was calculated by taking the difference of the amount of the substrate before the zeolite was added and the amount recovered in the solvent filtrate.

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