An organic sensitizer within Ti-zeolites as photocatalyst for the selective oxidation of olefins using oxygen and water as reagents

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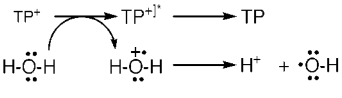
A new positive photocatalytic system comprising an organic dye within the micropores of a titanium zeolite is able to effect the catalytic dihydroxylation of alkenes using water and molecular oxygen as reagents; the dye acts as an antenna to absorb the energy of visible light, generating hydroxyl radicals from water; subsequently, the OH˙ radicals react with olefins in the presence of oxygen to form allylic hydroperoxides that in the presence of the Ti atoms of the zeolite promote the epoxidation of the alkene.

Photocatalysis applies the energy of light to effect chemical reactions. The energy of a blue photon (λ = 400 nm) is 71 kcal $\times$ mol^{-1}, enough to overcome most of the activation barriers of chemical reactions. Compounds considered chemically inert, such as water, may become reactive under photocatalytic conditions.

Up to now, photocatalysis has been almost exclusively limited to the degradation of pollutants in aqueous media,[1] but *positive* photocalysis being applied to the synthesis of organic compounds is more scarce.[2] Herein, we report a positive photocatalytic system that comprises 2,4,6-triphenylpyrylium ion (TP$^+$) encapsulated within the voids of tridirectional large-pore zeolites that absorbs visible light, transforming it into chemical energy. A second Ti catalytic site located in the walls of these molecular sieves promotes oxidation of an alkene using as reagent the hydroperoxides generated *in situ* in the photochemical process (Fig. 1).



Scheme 1

Zeolites are crystalline aluminosilicates whose structure contains strictly uniform cavities and channels of molecular dimensions called micropores.[3] The zeolite host cooperates in the success of the overall process, playing several crucial roles. Thus, TP$^+$ is not stable in H_2O where it undergoes rapid hydrolysis to 1,3,5-triphenylpent-2-ene-1,5-dione. This prevents the direct use of this sensitizer in aqueous media. In contrast, when encapsulated inside the cages of zeolites (TP-Z), the confined space provided by the host impedes the reaction of the heterocycle because it involves bulkier intermediates that simply would not fit in. As result, when entrapped inside the zeolite micropores TP$^+$ is completely stable in the presence of H_2O. In addition, the zeolite pores provide a polar reaction medium favorable for the initial photoinduced electron transfer between TP$^+$ excited state and water (Scheme 1). This oxidation transforms inert water into chemically agressive hydroxyl radicals. Evidence for the formation of OH˙ in this system has been previously obtained by laser flash photolysis.[5] In addition, trapping of OH˙ by 5,5-dimethyl-1-pyrroline *N*-oxide leads to a persistent N-centered radical detectable by conventional EPR spectroscopy.

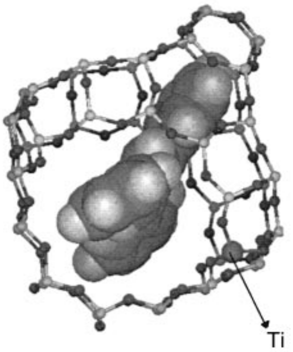
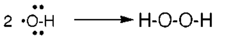


Fig. 1 Molecular modeling structure of TP,Ti-Zeolite bifunctional photocatalyst. The bulky TP$^+$ acting as light harvester is entrapped inside the zeolite cavities. The Ti atoms are bonded to the framework of the zeolite.

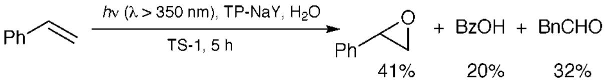
Normally, OH˙ radicals would destroy any organic photosensitizer. However, in the case of the TP-Z system, the restricted reaction cavity prevents this OH˙ attack. In fact, no bleaching of TP$^+$ was observed after an operation time of 100 h. Furthermore, the final product of the OH˙ chemistry in the TP-Z irradiation of pure water is H_2O_2, indicative of OH˙ coupling [eqn. (1)].



$$2\ \cdot\ddot{\underset{\cdot\cdot}{O}}\text{-H} \longrightarrow \text{H-O-O-H} \qquad (1)$$

Eqn. (1) is well-established in the γ-radiolysis of H_2O[6] but never occurs when there are alternate waste channels for OH˙ radicals. Fig. 2 shows an illustrative time-conversion plot for the concentration of H_2O_2 under these conditions.

The ability of TP-NaY sensitizer to generate a constant concentration of H_2O_2 has been exploited here for the epoxidation of styrene using titaniumsilicalite (TS-1) as co-catalyst, whereby styrene oxide is formed [eqn. (2)]. However,



(2)

the low photostationary concentration of H_2O_2 determines that the epoxidation step takes hours. This allows the occurrence of concomitant photochemical reactions leading to by-products (mainly benzoic acid and 2-phenylacetaldehyde).

This limitation was overcome by using TP-Z as a continuous source of OH˙ radicals to generate *in situ* organic hydroperoxides formed through hydrogen abstraction and subsequent trapping of the carbon-centered radical by O_2. Thus, when cyclohexene was present during the irradiation of a H_2O–MeCN slurry with TP-Z photocatalyst, 3-hydroperoxycyclohexene was formed (Scheme 2). This was confirmed by addition of PPh_3 after the photocatalytic irradiation. PPh_3 reacts quantitatively with organic hydroperoxides giving rise to the corresponding alcohol plus Ph_3P=O. The yield of hydroperoxycyclohexene can be quantitatively determined by iodometric titrations or, alternatively, by the amount of Ph_3P=O formed. Control experiments showed that the direct reaction of cyclohexene with TP$^+$ in its excited state does not occur, in agreement with the high cyclohexene oxidation potential (2.14 V *vs.* SCE).

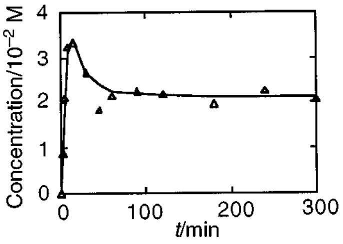
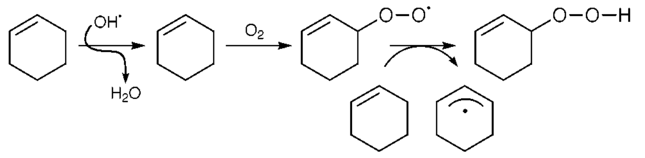


Fig. 2 Hydrogen peroxide concentration profile upon irradiation (visible light, $\lambda > 350$ nm) of TP-NaY (100 mg) in water.



Scheme 2

Large pore Ti molecular sieves are efficient catalysts for the selective epoxidation of alkenes by organic hydroperoxides.[7] We have exploited the ability of TP-NaY to generate a significant concentration of hydroperoxides from light and H_2O–O_2 and coupled it with the subsequent epoxidation converting the whole process in a one-pot reaction.

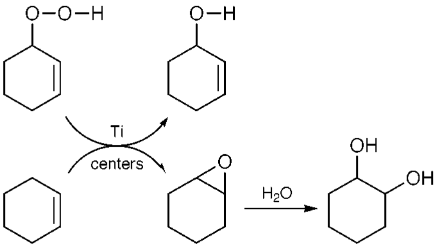
Two different strategies have been explored. The simplest one consists in using a mechanical mixture of two molecular sieves, one containing TP^+ as photocatalyst and the second one having Ti atoms as epoxidation sites. Table 1 summarizes the results that have been achieved using a system containing a mixture of TP-NaY and Ti-β or Ti-MCM-41.[7–10] The major difference between the latter two epoxidation catalysts is the geometry and dimensions of the internal voids, both having in common their relative hydrophocity that favors the preferential adsorption of organic compounds.[7] The structure of β zeolite defines a tridirectional network of oval cages (11 Å major axis) while MCM-41 is formed by an array of hexagonal channels (30 Å diameter).

In agreement with the chemical literature,[7] Al-free Ti-MCM-41 was found more active than Al-free Ti-β. The higher activity of Ti-MCM-41 is easily rationalized based on the larger dimensions of its pores that suit better to the size of the reagents involved in the process. When the TP-NaY/Tiβ mixture was reused in a second and third experiment with fresh feed a notable loss of activity was observed (see Table 1, footnotes *c* and *d*). However, this decay in the efficiency of the photocatalytic mixture is not caused by the bleaching of TP^+ since no changes were observed in the characteristic UV/vis absorption of the solid. Rather, it is more likely that the deactivation is due to blocking of the pores by oligomers or bleaching of Ti atoms out of the Ti-β framework.

Table 1 Results after 4 h irradiation (125 W Hg lamp through Pyrex) at room temperature of cyclohexene (2 ml) in a mixture of MeCN (2 ml)–H_2O (1 ml) in the presence of the corresponding photocatalyst (500 mg, 4% loading of TP^+)

	Products/mg		
Photocatalyst[a]	cyclohexane-1,2-diol	cyclohex-2-enol	cyclohex-2-enone
TP-NaY[b]	1.5	6.8	13.9
TP-NaY/Ti-β	10.9	23.7	16.8
TP-NaY/Ti-β[c]	4.5	13.9	13.8
TP-NaY/Ti-β[d]	2.2	13.6	7.4
TP-NaY/Ti-MCM-41	13.4	17.6	18.7
TP, Ti-β	20.2	39.7	11.5

[a] Blank controls under Ar atmosphere, in the dark or in the absence of TP-Y did not lead to any product. [b] In the absence of Ti-containing co-catalyst. [c] Second run reusing TP-NaY/Ti-β with fresh reagents. [d] Third run reusing TP-NaY/Ti-β with fresh reagents.



Scheme 3

On the other hand, according to Scheme 3, cyclohex-2-enol and cyclohexane-1,3-diol would be concurrently formed in the oxidation step while cyclohex-2-enone would arise from the subsequent overoxidation of cyclohex-2-enol.

Even though the TP-NaY/Ti-zeolite mixtures act as photocatalysts, their activity and selectivity are far from optimal. In order to increase the efficiency of the overall photocatalytic reaction, a fully-integrated approach was explored. It consists of the preparation of a single bifunctional photocatalyst that contains the two centers necessary for the process in the closest possible proximity. For this purpose, we have carried out the ship-in-a-bottle synthesis of TP^+ in a Ti-Beta zeolite following the procedure reported for zeolite Y.[9] As can be seen in Table 1, the efficiency of the overall dihydroxylation process is almost doubled using this novel TP, Ti-β photocatalyst compared to the mechanical mixture of the two separate components. This higher activity of TP,Ti-β for the production of cyclohexane-1,2-diol can be understood as a consequence of the spatial arrangement of the sites that reduces the chances for undesirable decomposition of hydroperoxy cyclohexene.

To establish a valid comparison of the efficiency of the TP, Ti-β photocatalysis, the autooxidation of cyclohexene (2 ml) initiated by azoisobutyronitrile (30 mg) was also carried in MeCN (2 ml) in the presence of Ti-β (200 mg) bubling air through the solution. After 5 h reaction, only 4.5 mg of cyclohexane-1,2-diol was formed. This value is smaller than those achieved with the TP,Ti-β photocatalysis (see Table 1).

Even though further improvements are still needed, herein we have shown that TP,Ti-β acts as a new *positive* photocatalytic system that by using photons promotes the dihydroxylation of cyclohexene using water and oxygen as reagents. The overall process occurs within the pores of zeolites, whose rigid structure embeds and protects the active centers, cooperating in the process in a way reminiscent of the quaternary structure of enzymes around a prostetic group.

Notes and references

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