Photooxidation of Hydrocarbons on Porphyrin-modified Titanium Dioxide Powders

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A composite catalyst consisting of an iron porphyrin covalently linked to TiO_2 shows a new reactivity in the photochemical mono-oxygenation of hydrocarbons under mild conditions, with respect to the porphyrin and TiO_2 used separately.

The functionalization of hydrocarbons is a topic of great interest and is currently the object of intense research in several laboratories.[1] We report herein on the photocatalytic oxygenation of cyclohexane and cyclohexene using a composite catalyst consisting of an iron(III)-*meso*-tetrakis(sulfonatophenyl)porphyrin [Fe^{III}(tpps)] covalently linked to titanium dioxide. We show that compared with both TiO_2 and the porphyrin in the solution phase, the new catalyst features a novel reactivity.

The study of surface-modified semiconductors itself has long been the object of considerable interest. Earlier investigations mainly addressed the problem of sensitization of large band gap semiconductors[2] or the stabilization of low band gap ones against photocorrosion.[3] While these continue to be important research topics,[4] recent work also aims at modifying semiconductor surfaces for photosynthetic purposes.[5]

The oxidation of alkanes and alkenes on dispersed semiconductors has been previously described.[6] Recently, we reported that the photochemical method can be used to oxidize cycloalkanes with O_2 under mild conditions in the presence of catalytic amounts of Fe^{III}-porphyrins.[7a]

The linkage of Fe^{III}(tpps) to TiO_2 (Degussa P25) has been carried out as described by Hong *et al.*[8] for the attachment of phthalocyanines to oxide supports. In this procedure the surface is first modified using triethoxyaminopropylsilane (TiO_2-sil) and then allowed to react with the porphyrin whose-SO_3 groups have previously been converted into -SO_2Cl. The surface coverage by the complex was estimated† to be 30%, in accord with the data of Hong *et al.*[8] In a typical

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† The determination of the % coverage has been carried out by demetallation of the anchored porphyrin. A known amount of the modified catalyst was refluxed in concentrated H_2SO_4 for one night. After separation of the TiO_2 and washing with H_2SO_4, the amount of iron was determined by atomic absorption spectroscopy. Based on the analysis, we calculated 5×10^{18} molecules of porphyrin per g of TiO_2; since one molecule occupies *ca.* 400 Å and the TiO_2 surface area is 55 $m^2 g^{-1}$, the coverage by the porphyrin is estimated to be *ca.* 30%.

Table 1 Photocatalytic oxidation of cyclohexane and cyclohexene on TiO_2 and surface modified TiO_2 powders

Catalyst	Substrate	Products	IMPP	Porphyrin turnover[a]
TiO_2	Cyclohexane	Cyclohexanone	0.09	
		Cyclohexanol	[b]	
		CO_2	0.024	
	Cyclohexene	Cyclohexenone	0.57	
		Cyclohexenol	0.27	
		Cyclohexeneoxide	0.01	
		CO_2	0.004	
TiO_2-sil	Cyclohexane	Cyclohexanone	[b]	
		Cyclohexanol	[b]	
		CO_2	[b]	
	Cyclohexene	Cyclohexenone	0.25	
		Cyclohexenol	0.14	
		Cycloheheneoxide	0.01	
		CO_2	0.001	
TiO_2-sil-Fe^{III}(tpps)	Cyclohexane	Cyclohexanone	0.03	50
		Cyclohexanol	0.01	14
		CO_2	[b]	
	Cyclohexene	Cyclohexenone	0.79	810
		Cyclohexenol	0.48	490
		Cyclohexeneoxide	0.01	9
		CO_2	0.0027	3

[a] Amount of product/destroyed porphyrin. [b] Below our revelation capabilities.

experiment the powder catalyst was suspended (4 mg ml^{-1}) in the O_2-saturated neat hydrocarbon and irradiated at $\lambda = 365$ nm for 3–4 h. The yields are given as the ratio of incident monochromatic photons to product efficiencies[5c] (IMPP). Experiments carried out at different wavelengths showed that the product yields matched the adsorption spectrum of TiO_2, indicating that the semiconductor is the photochemically active species. In Table 1 the results obtained with the derivatized TiO_2 and those obtained with the unmodified TiO_2 are compared. The latter is known to be an active catalyst in the oxidation of hydrocarbons including cyclohexane and cyclohexane. In agreement with the literature data,[6] the oxidation of cyclohexane on the unmodified TiO_2 leads essentially to cyclohexanone and CO_2. When the reaction is carried out under O_2 (1 Torr = 133.322 Pa) products are formed in traces and we observe dicyclohexyl (from cyclohexyl radicals) in addition to cyclohexanone. The formation of dicyclohexyl has seemingly not been reported previously on TiO_2.

The data in Table 1 show a marked loss of activity when TiO_2 is derivatized with the silane only. On the other hand, a new interesting reactivity is observed when also Fe^{III} (tpps) is linked to the surface in that we obtain cyclohexanol in addition to cyclohexanone. We point out that the IMPP value for the ketone formation in the system Fe^{III}(tpps)–cyclohexane is about two orders of magnitude higher than that observed using the same porphyrin in homogeneous phase experiments.[7a]

In the oxidation of cyclohexene the TiO_2-sil-Fe^{III}(tpps) system is markedly more efficient than both TiO_2 and the porphyrin in solution,[7] and the amount of cyclohexenol among the products is higher (Table 1).

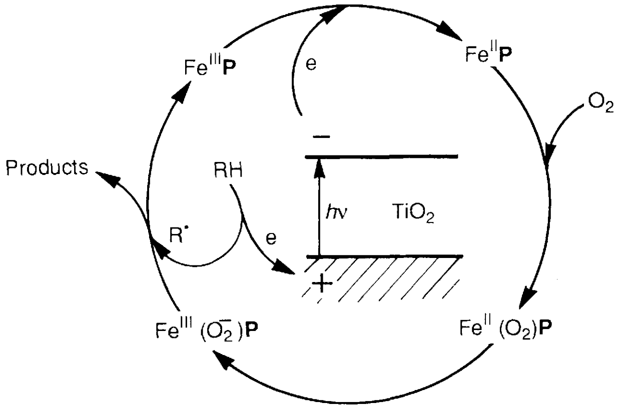
It is noteworthy that the porphyrin turnovers reported in Table 1 are significantly higher than those observed when the porphyrin is used as the photocatalyst in the homogeneous phase.[7] In this case, to achieve turnover values of this magnitude it is normally necessary to employ protected porphyrins such as the perhalogenated ones. We expect that the use of anchored porphyrins, which are sterically protected, will further improve the turnover; experiments in this direction are currently under way.

An inspection of Table 1 shows that the complete degradation of the hydrocarbons to CO_2 is inhibited on the modified TiO_2, *i.e.* the oxidizing power of TiO_2 decreases when it is derivatized as proposed here.

Since the silanization drastically deactivates the TiO_2, we infer that the porphyrin complex is responsible for the observed reactivity of the system TiO_2-sil-Fe^{III}(tpps). We must admit that, in this case, the porphyrin creates new active surface sites, which are entirely different from those of TiO_2, and the reaction mechanism needs to be rediscussed. In the following we illustrate experiments directed at the identification of the processes occurring at these sites.

The capture of the photogenerated electrons by Fe^{III} to give Fe^{II} makes the porphyrin an electron-acceptor surface state. Hong *et al.*[8] previously reported that a Co-phthalocyanine linked to TiO_2 acts as an efficient electron acceptor. We demonstrated the formation of Fe^{II} by carrying out the irradiation of TiO_2-sil-Fe^{III}(tpps) in the absence of O_2 and in the presence of pyridine which is known to stabilize Fe^{II}.[9] Indeed, we observed the growth of the bands of the Fe^{II}-pyridine complex at 440, 548 and 558 nm in the diffused reflectance spectrum of TiO_2-sil-Fe(tpps). Chemical reduction with dithionite gave the same spectral variations.

As recently pointed out by Gerischer and Heller[10] the reduction of O_2 on the particles is essential in the overall process since it removes the excess of electrons and maintains the oxidation of the organic substrate. It is also reported that



Scheme 1 Fe^{III}**P** = Fe^{III}(tpps)

the products of O_2 reduction may be reactive toward the radical intermediates of the oxidation process.[10]

The ability of metal porphyrins to catalyse the reduction of O_2 at electrodes is well documented.[11] Fig. 1 shows voltammetry curves for the reduction of O_2 on both unmodified and derivatized TiO_2 polycrystalline electrodes. Although the data refer to aqueous solutions, they can be considered indicative of a trend. It is apparent that silanization causes a marked loss of activity for the reduction of O_2. Attachment of the porphyrin to the silane layer causes an almost complete recovery of activity. Apparently, the covalently bound porphyrin cannot improve the electrocatalytic activity of TiO_2 for O_2 reduction; this is because a large fraction of the surface is still covered by the inactive silane layer. We stress, however, that the point of interest at this stage of the research is that the active sites for the reduction of O_2 can be clearly identified with the porphyrin centres. It is well known that the metal centre of the porphyrin complex in its reduced form can rapidly coordinate a O_2 molecule to yield the corresponding superoxide complex.[12] This should be relatively stable if the medium is the pure hydrocarbon. Although the formulation of a mechanism is premature, it is likely that the Fe^{III}-superoxide complex plays a fundamental role in the mono-oxygenation of hydrocarbons on TiO_2-sil-Fe(tpps), as illustrated in Scheme 1.

The high IMPP values observed in this system may then be attributed to the high reduction efficiency of Fe^{III} by the conduction band electrons; the illuminated semiconductor then acts as a source of electrons. In contrast, reduction of Fe^{III} in well characterized homogeneous processes involving the porphyrin is due to a less efficient axial ligand to metal charge transfer.[7,13]

One way in which the superoxide may be involved in the mechanism is in the formation of a hydrocarbon radical–peroxide complex as has been proposed for the homogeneous-phase oxidation of hydrocarbon photocatalysed by metalloporphyrins:[7] this complex is the intermediate that can lead to the ketone or the alcohol.[14] There are probably several other alternative routes and experiments are underway to improve our understanding.

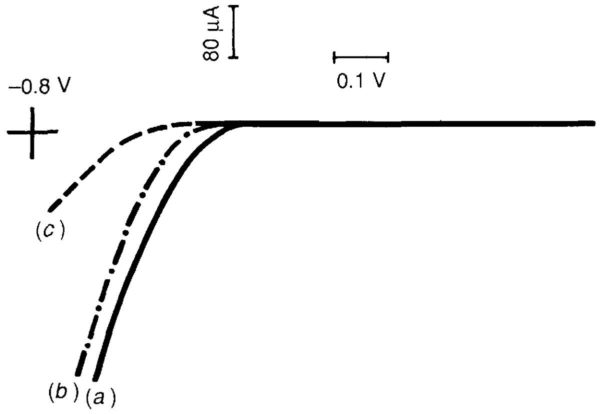


Fig. 1 Reduction of oxygen on TiO_2 and modified TiO_2 electrodes in 0.2 mol dm^{-3} $NaClO_4$. Sweep rate: 20 mV s^{-1}. (*a*) TiO_2, (*b*) TiO_2-sil-Fe^{III}(tpps) and (*c*) TiO_2-sil.

The system proposed here is a hybrid one consisting of catalysts (the porphyrin and TiO_2) able to function separately in the photooxidation of hydrocarbons. In comparison with unmodified TiO_2 we note (*i*) the production of cyclohexanol and an increase in the yield of mono-oxygenation products of cyclohexene, (*ii*) the creation of better defined sites for O_2 reduction (the anchored porphyrin). In comparison with the porphyrin in the solution phase, we note (*iii*) higher yields in the oxidation products, which quite likely reflect an increased efficiency of photoreduction of Fe^{III} to Fe^{II} for the anchored complex, (*iv*) higher turnover numbers with respect to the same porphyrin in the solution phase. We also point out that semiconductor/porphyrin photosystems may be of interest in the research on haemoprotein models capable of mimicking the features of biological processes: *e.g.* cytochrome P450 is known to oxidise cyclohexane to cyclohexanol.

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