# Alkene Oxidation in Water using Hydrophobic Silica Particles Derivatized with Polyoxometalates as Catalysts

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An insoluble catalytic assembly consisting of a silicate xerogel covalently modified with phenyl groups and quaternary ammonium–polyoxometalate ion pairs was used to catalyse the oxidation of alkenes with 30% aqueous hydrogen peroxide in the absence of an organic solvent.

Catalytic oxidation of hydrocarbons using environmentally benign oxidants instead of stoichiometric reagents common in the field of synthetic organic chemistry has received significant research attention in recent years. In this context, 30% aqueous hydrogen peroxide is particularly attractive since water is the byproduct obtained upon oxygen donation.[1] Many catalysts have been developed and investigated. Of particular interest are those having high activity, selectivity and stability such as $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$,[2] $CH_3ReO_3$,[3] and $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$,[4] although this is certainly not an exhaustive listing. Since simple hydrocarbons are not miscible with aqueous hydrogen peroxide, reactions are either carried out in polar solvents such as acetonitrile or acetic acid or in two-phase systems generally using chlorinated hydrocarbons and quaternary ammonium–catalyst ion pairs to maximize surface contact and reactivity.[5] Scaling-up of procedures using such solvents will require complex separations and/or effluent treatment so that the solvents themselves will not be ecologically significant.

An important goal, therefore, in hydrocarbon oxidations is to carry out reactions without addition of organic solvent so that oxidations may take place only in the presence of the aqueous oxidant phase, in this case hydrogen peroxide, and the neat hydrocarbon substrate, for example alkenes. The strategy we have applied is to create a multi-functionalized, insoluble, silicate-based particle, capable of effective adsorption of the alkene substrate and having catalytic centres at the particle and adsorbed substrate–water interface (Fig. 1). Effective adsorption of the alkene substrate was achieved by preparing hydrophobic silicate xerogels with covalently attached phenyl units. Catalytic centres were introduced by connecting quaternary ammonium cations to the xerogel and using anionic polyoxometalates, $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ **1** and $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ **2** as catalytically active species. Thus, the silicate particles were prepared by copolymerization of $Si(OEt)_4$, $PhSi(OEt)_3$ and $[R^3O)_3SiR^1N^+R^2Me_2Cl^-$† using the sol–gel technique[6] followed by addition of the polyoxometalate to the gel and evaporation of the solvent to obtain the required silicate xerogel particles.‡

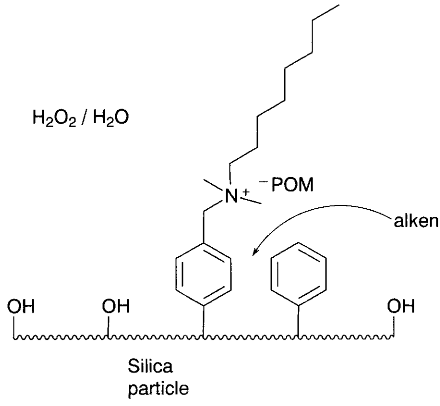

**Fig. 1** A simplified representation of the multi-functionalized catalytic particle in hydrocarbon–water mixtures

The effectiveness of the catalytic particles was tested in the oxidation of alkenes. The importance of the phenyl groups and the identity of the quaternary ammonium group were tested first. Thus, 1 mmol of cyclooctene, and 2 mmol of 30% aqueous $H_2O_2$ were mixed at room temperature for 24 hours with the silicate xerogel containing 0 or 10 mol% phenyl groups and 0.5 mol% $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ ($SiO_2$-**1** or 10% $PhSiO_2$–$SiO_2$-**1**). The cyclooctene : $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ ratio was 200 : 1. The results§ in Fig. 2 clearly show that the combined presence of phenyl units and the use of the octyldimethyl substituted ammonium salt brings about the maximum catalytic activity. This result can be interpreted as follows. The trimethylpropylammonium cation is too hydrophilic to allow the approach of cyclooctene to the active peroxo centre. The dodecyldimethylbenzylammonium cation is of a highly surfactant nature allowing optimum mixing of water and alkene at the catalytic centre thereby yielding significant activity. However the increased hydrophobicity of the xerogel particle through addition of phenyl units has no effect. Only in the case of the octyldimethylbenzylammonium salt is there a synergistic effect of the addition of phenyl units to the xerogel. The same effect was observed using the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ polyoxometalate attached to the octyldimethylphenylammonium group. For example at a ratio of cyclooctene to $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ of 500 : 1 a 19% conversion was observed without phenyl units ($SiO_2$-**2**) whereas a 58.6% conversion was obtained with 20% phenyl units (20% $PhSiO_2$–$SiO_2$-**2**) using the same reaction conditions as described above. It is important also to point out that reactions carried out using $(Bu^n_4N)_3\{PO_4[W(O)(O_2)_2]_4\}$ dissolved in the reaction system in the absence of catalytic particles or encapsulated in a xerogel particle[7] showed at best very limited catalytic activity (0–2 turnovers). The scope of the reaction is general for many alkenes as may be observed in Fig. 3. Thus, using the $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ compound attached to catalytic particles, alkenes are oxidized at selectivities similar to those observed in the usual two-phase, *e.g.* 1,2-dichloroethane–water systems[4] although activities are somewhat lower; however the reactions have yet to be optimized.

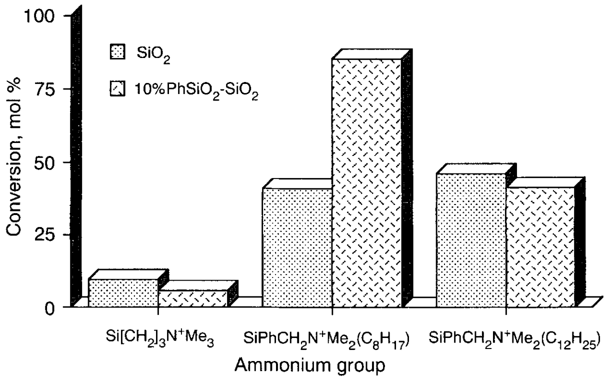

**Fig. 2** The activity of the catalytic particles in the oxidation of cyclooctene with aqueous 30% $H_2O_2$. *Reaction conditions*: 1 mmol of cyclooctene, 2 mmol of 30% $H_2O_2$, 0.005 mmol of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ attached to silicate xerogels, room temp., 24 h. The results shown are in each case an average of three runs with a maximum deviation of ±2 mol% conversion.

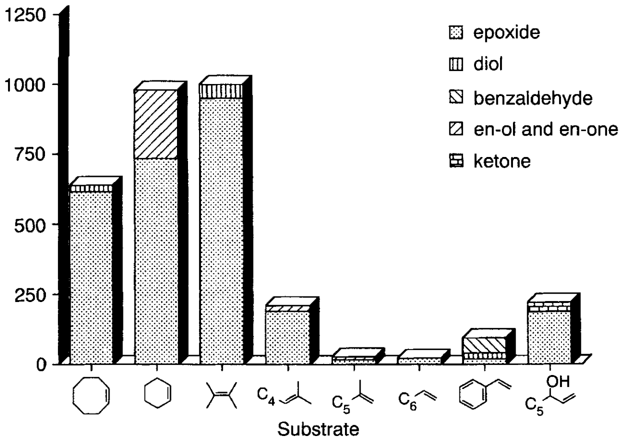

**Fig. 3** Oxidation of alkenes with aqueous 30% $H_2O_2$. *Reaction conditions*: 1 mmol of substrate, 2 mmol of 30% $H_2O_2$, 0.001 mmol of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ attached to a silicate xerogel (0.16 g) consisting of 20 mol% $PhSiO_2$, 2 mol% $(Me[CH_2]_7)Me_2N^+PhCH_2SiO_2$ and 78 mol% of $SiO_2$ (20% $PhSiO_2$–$SiO_2$-**2**), room temp., 24 h.

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## Footnotes

† Three different quaternary ammonium substituted siloxanes, $(R^3O)_3SiR^1N^+R^2Me_2Cl^-$ were used. One was $(EtO)_3Si[CH_2]_3N^+ Me_3Cl^-$, purchased from Aldrich. The others, $(MeO)_3SiPhCH_2N^+Me_2([CH_2]_nMe)Cl^-$ ($n$ = 7, 9) were prepared by the reaction of 10 ml (0.4 mol) of $(MeO)_3SiPhCH_2Cl$ with a equimolar amount of octyl- or dodecyldimethylamine dissolved in 60 ml of light petroleum (bp 100–120 °C) at reflux overnight. After cooling the product was filtered off (yield 40–70%) and used directly.

‡ Silicate xerogels were synthesized containing 2 mol% of the quaternary ammonium derivative by mixing together 130 mmol of $Si(OEt)_4$ and $PhSi(OEt)_3$ at the desired molar ratios, 2.6 mmol of $(R^3O)_3SiR^1N^+R^2Me_2Cl^-$ in 75 ml of EtOH; 20 ml of water and 0.7 ml of dibutyltin dilaurate (polymerization catalyst) were added and the mixture was held at 60 °C for 3 h. The solution was cooled and either 0.65 mmol of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$,[8] or 0.17 mmol of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ (ref. 9) were added as aqueous solutions. The solvents were slowly evaporated off (24–48 h) and the samples dried at 50 °C overnight. In this manner catalytic silicate particles containing 0.5 mol% of $\{PO_4[W(O)(O_2)_2]_4\}^{3-}$ and 0.133 mol% of $[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$ were obtained.

§ At the end of the reaction the products were analysed and quantified by GLC [HP5890; 15 m methylsilicone (RTX-1), 0.32 mm id, 0.025 μm coating capillary column, He carrier gas, flame ionization detector] with authentic samples as references.

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