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Hydroxylation of Alkanes Catalyzed by Manganese Tetraphenylporphyrin Immobilized on Imidazole-modified Silica Gel

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Immobilization of Mn(TPP)Cl (TPP = tetraphenylporphyrin) onto 3-imidazolylpropyl-modified SiO_2 resulted in enhancement of its activity for hydroxylation of cyclohexane; the support prevented the complex from forming a dimer leading to oxidative destruction.

While biomimetic studies of cytochromes P-450 have received much attention, there are relatively few systems which perform alkane hydroxylation with high activity in terms of turnover number under relatively mild conditions. Recently Mn porphyrins have been reported to catalyze conversions of alkanes into alcohols and ketones by using H_2O_2 as an oxidizing agent and in the presence of imidazole,[1)] where the prevention of the formation of μ-oxo dimers by steric hindrance increases catalytic capability by decreasing the rate of oxidative destruction.[2)] It seemed, however, that the main disadvantage of those catalyst system is the difficulty in synthesizing the sterically hindered porphyrins.[3)] It occurred to us that rigid inorganic supports should be effective[4)] in preventing catalyst deactivation caused by dimerization of sterically uncrowded porphyrins such as TPP (TPP = tetraphenylporphyrin). Here we report the hydroxylation of cyclohexane catalyzed by Mn(TPP) immobilized on silica modified with imidazoles.

Im/SiO_2 (Im = imidazole) and $NMIm/SiO_2$ (NMIm = N-methylimidazole) were prepared by impregnating SiO_2 (Fuji Davison ID) with Im and NMIm, respectively, from ethanolic solution. A SiO_2 containing 3-imidazolylpropyl groups bonded to surface atoms of silicon was prepared according to the method described in the literature[5)] and designated as $(Im)SiO_2$. Four types of supported catalysts i.e., $Mn(TPP)Cl/SiO_2$, $Mn(TPP)Cl/Im/SiO_2$, $Mn(TPP)Cl/NMIm/SiO_2$, and $Mn(TPP)Cl/(Im)SiO_2$ were prepared by impregnation with Mn(TPP)Cl from its $CHCl_3$ solution. In the standard procedure of the cyclohexane hydroxylation, aqueous H_2O_2 was injected by a syringe pump to a stirred suspension of the catalyst in cyclohexane.

Table 1 shows the performances of the catalysts for the hydroxylation of cyclohexane by H_2O_2. The product yields are based on Mn(TPP)Cl. The $(Im)SiO_2$-supported catalyst exhibited the highest turnover of cyclohexane to cyclohexanol and cyclohexanone of 42.8 at 50 °C, which was 31 times as high as that of the SiO_2-supported one. Cyclohexanone seems to be formed by way of cyclohexanol. The catalyst supported on Im/SiO_2 and $NMIm/SiO_2$ showed very little activity; simple impregnation with these imidazoles was ineffective in promoting the activity and the imidazolyl group must be chemically bonded to SiO_2. Without $(Im)SiO_2$,

Table 1. Mn catalyzed oxidation of cyclohexane[a)]

Catalyst	Yield (mol-prod./mol-Mn) cyclohexanol	 cyclohexanone
$Mn(TPP)Cl/SiO_2$	0.9	0.5
$Mn(TPP)Cl/Im/SiO_2$	1.2	1.1
$Mn(TPP)Cl/NMIm/SiO_2$	0.9	0.6
$Mn(TPP)Cl/(Im)SiO_2$	32.3	10.5
Mn(TPP)Cl[b]	n.d.[c]	n.d.[c]
Mn(TPP)Cl-Im[b]	n.d.[c]	n.d.[c]

a)Cyclohexane 93 mmol, H_2O_2 2.5 mmol, catalyst 2 .0 g (Mn 0.01 mmol, imidazoles/Mn = 200±5), 50 °C, 120 min. b) Carrier-free.
c) Not detected.

Mn(TPP)Cl proved to have no activity irrespective of whether imidazole was present or not, suggesting that, in homogeneous system, dimerization of complexes rapidly occurred, resulting in oxidative destruction of the catalyst. A control experiment performed under nitrogen gave almost identical results to those obtained under aerobic conditions, indicating that the molecular oxygen is not significantly involved in this oxidation. The activity of other metalloporphyrins, namely, Fe(TPP)Cl, Co(TPP), Ni(TPP), and Cu(TPP), supported on $(Im)SiO_2$ was found to be negligible.

A significant difference between the diffuse reflectance visible spectra of $Mn(TPP)Cl/(Im)SiO_2$ and $Mn(TPP)Cl/SiO_2$ was found in the Soret band. The $Mn(TPP)Cl/(Im)SiO_2$ showed an absorption maximum at about 475 nm; the shift of about 6 nm to shorter wavelength might be indicative of imidazole ligation to Mn(TPP)Cl. Yuan and Bruice interpreted similar spectral changes in the Soret band region in terms of the formation of the bis complex of imidazole with Mn(TPP)Cl monomer.[6)] Thus immobilization of Mn(TPP)Cl through coordination to SiO_2-bonded imidazole should give rise to site isolation and so inhibit deactivation through dimerization on addition of H_2O_2.

The efficiency of the oxygen atom transfer from H_2O_2 to other hydrocarbons over $Mn(TPP)Cl/(Im)SiO_2$ was also investigated. In the case of adamantane the hydroxylation of tertiary C-H bonds were predominant over that of secondary ones, the normalized tertiary/secondary ratio being 5.4. This suggests that the reaction proceeds through a mechanism different from a Fenton-type free radical oxidation in which typical ratios exceed 20.[7)]

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