Manganese Porphyrins Supported on Montmorillonite as Hydrocarbon Mono-oxygenation Catalysts: Particular Efficacy for Linear Alkane Hydroxylation

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A supported Mn–porphyrin catalyst has been prepared by immobilisation of the tetracationic Mn [meso-tetra (4-*N*-methylpyridiniumyl)porphyrin]Cl^{4+} on montmorillonite, and is found to be efficient for alkene epoxidation and alkane hydroxylation by PhIO, with a higher ability to oxidize alkanes, and in particular short linear alkanes, than corresponding homogeneous or silica-supported Mn–porphyrin catalysts.

Many hydrocarbon oxidation systems that mimic cytochrome P-450-dependent mono-oxygenases and utilise iron– or manganese–porphyrins as catalysts and various single oxygen atom donors, such as PhIO, ClO^-, or H_2O_2, have been reported.[1] The high efficiency of some of these systems makes them potentially useful for preparative oxidations in organic chemistry. For that purpose, immobilisation of metalloporphyrin catalysts on inorganic supports appears to be a good way to render them more practical and maybe to improve their catalytic activity and selectivity. Recent results show that charged Mn–porphyrins adsorbed on silica or alumina were good epoxidation catalysts and that cationic porphyrins adsorbed on silica were especially efficient for alkane hydroxylation.[2] It has also been shown that Mn–porphyrins inserted into zeolites present interesting substrate specificities and regioselectivities for linear alkane hydroxylation.[3] Clay minerals appear as another class of interesting supports for catalysts.[4] They have been found to bind metalloporphyrins,[5—7] but clay-supported metalloporphyrins have never been used so far as oxidation catalysts.

This Communication describes a new oxidation catalyst involving a Mn–porphyrin supported on montmorillonite, which is very easy to prepare, that can be used without degradation in various solvents such as CH_2Cl_2, CH_3OH, or H_2O, and shows a particular efficacy for the hydroxylation of short linear alkanes, when compared with corresponding homogeneous catalysts or to Mn–porphyrins supported on silica.

The tetracationic chloro{*meso*-tetra(4-*N*-methylpyridinio)-porphyrinato}manganese(III) tetrachloride, [Mn(tmpyp)Cl],[8] very strongly binds to montmorillonite. A typical preparation of the clay supported Mn–porphyrin, ClaypMn, involved the stirring of 2 g of montmorillonite (KSF Fluka, after exchange of its interlamellar cations by Na^+)[9] with 1 g of Mn(tmpyp)Cl in 50 ml H_2O at 100 °C for 24 h, according to a procedure previously reported for the immobilisation of cobalt porphyrins in montmorillonite.[7] Filtration and washing with CH_3OH followed by extensive washings with CH_2Cl_2 and CH_3CN, results in a solid that is found to retain the adsorbed Mn–porphyrin when put in suspension in CH_3CN even after one week. The UV–VIS spectrum of this solid exhibited two intense peaks at 471 and 496 nm corresponding to the Mn^{III}–porphyrin in two different environments, but no peak corresponding to the free-base porphyrin was seen. Two Soret peaks have previously been observed upon insertion of a Co^{II}–porphyrin into montmorillonite.[7] As in the present case, one of these peaks was very similar to that of the starting Co–porphyrin whereas the second one was red-shifted by *ca.* 20 nm. Elemental analysis (Mn) of the solid showed that it contained about 5% (*w* : *w*) of bound Mn–porphyrin. Upon washing with H_2O, it released not more than 10% of Mn–porphyrin and then retained completely the bound metalloporphyrin even after extensive washing with H_2O for several days. It was, thus, possible to use the ClaypMn catalyst for oxidation reactions not only in CH_2Cl_2 or CH_3CN but also in very polar solvents such as CH_3OH or H_2O without release of the tetracationic Mn–porphyrin, which was not the case for the previously described silica-supported Mn–porphyrins.[2] It is noteworthy that montmorillonite-supported monocationic Mn–porphyrins, like Mn(tpp) (tpp = tetraphenyl porphyrin) $CF_3SO_3^-$, prepared under similar conditions released almost all their Mn–porphyrins when suspended in CH_3CN.

Table 1. Oxidation of alkanes by PhIO catalysed by Mn(tmpyp)Cl supported on montmorillonite (ClaypMn.)[a]

Alkane	Total yield (%)[b]	Alcohol(s)[c] yield (%)[b]	Ketone(s)[d] yield (%)[b]	Ol : one ratio[b]
Cyclo-octane	65 (17)	53 (5)	6 (6)	8.8
Cyclohexane	43 (8)	35 (4)	4 (2)	8.8
Adamantane	61 (8)	57 (7)	2 (0.5)	
Heptane	49 (3)	41 (1)	4 (1)	10.3
Pentane[e]	29	21 (1)	4	5.2

[a] Conditions: alkane: PhIO: Mn = 800 : 20 : 1 (equivalent concentration of supported catalyst: 1.5 mM) in 1 ml $CH_3CN : CH_2Cl_2 = 2 : 1$, 1 h at 20 °C under argon. [b] Yields based on starting PhIO. For total yields, it was assumed that 2 mol of PhIO were necessary for ketone formation. Results obtained with Mn(tmpyp)Cl alone in the *absence of clay are given in parentheses*; identical conditions were used except that 10% MeOH was added to solubilize the porphyrin (see also ref. 2). Analysis of products was made by GC on a FFAP (10%) column by comparison with authentic samples; yield determination was made using calibration curves with acetophenone as internal standard. [c] Alcohols formed: cyclo-octanol, cyclohexanol, 1- and 2-adamantanols (52 and 5%), heptan- 2-, 3-, and 4-ol (relative proportions: 37, 42, and 20%), and pentan- 1-, 2-, and 3-ol (relative proportions: 4, 61, and 35%). [d] Ketones formed: cyclo-octanone, cyclohexanone, 2-adamantanone, -2-, -3- and heptan-4-ones, and -2- and pentan-3-ones (relative proportions of the heptanones and pentanones identical to those of the corresponding alcohols). [e] Pentane oxidation was done in pure CH_2Cl_2 because of problems in the determination of pentanones by GC owing to superimposition with the peak of CH_3CN. It is noteworthy that yields obtained in pure CH_2Cl_2 were lower than those obtained in $CH_3CN : CH_2Cl_2$. For instance, the total yield for heptane oxidation was 38% in pure CH_2Cl_2 instead of 49% in $CH_3CN : CH_2Cl_2$. A similar 10% decrease of the pentanols yield was observed for pentane oxidation in pure CH_2Cl_2.

A suspension of ClaypMn in $CH_3CN : CH_2Cl_2$ (2 : 1) acted as a good catalyst for cyclo-octene epoxidation by PhIO leading to an almost quantitative reaction within less than 1 h (cyclo-octene: PhIO: Mn = 800 : 20 : 1) at 20 °C. In the presence of the claypMn suspension and under identical conditions, reaction of PhIO with various alkanes such as cyclo-octane, adamantane, cyclohexane, heptane, and pentane led to good yields of alcohols and ketones within 1 h at 20 °C (Table 1). These yields varied from 30 to 65% as a function of the alkane structure. The two components (clay and Mn–porphyrin) of ClaypMn were found to be essential since, under identical conditions, the clay in the absence of Mn–porphyrin was almost inactive (yields lower than 2%) and the Mn–porphyrin, Mn(tmpyp)Cl,[10] in the absence of clay, gave much lower yields (between 3 and 17%, see values in parentheses of Table 1) as previously reported.[2] It is noteworthy that the ClaypMn catalyst appeared to be stable under working conditions, as at least four successive additions of PhIO to the heptane oxidation medium led to very similar alcohol and ketone yields, and as the ClaypMn catalyst obtained by filtration and washing with CH_3CN at the end of a heptane oxidation experiment was found to be as active as the starting catalyst.

The regioselectivities observed for the oxidation of adamantane, heptane, and pentane were almost identical to those previously described for the same tetracationic Mn–porphyrin supported on silica (SiO_2pMn)[2] under identical conditions. However, for all the studied alkanes, total yields obtained with ClaypMn were higher than those obtained with SiO_2pMn[2] (yields increase to between 10 and 20%). This

Table 2. Relative reactivity between pentane and other alkanes in oxidations catalysed by ClaypMn or SiO_2pMn.

	Pentane/alkane reactivity[a]		
Catalyst	Adamantane	Cyclo-octane	Heptane
ClaypMn	0.35	0.3	1.8
SiO_2pMn	0.05	0.19	1.3

[a] Ratio between the oxidation yields [alcohol(s) + ketone(s)] obtained for pentane and for another alkane in competition experiments. Conditions: pentane : alkane : PhIO: Mn = 800 : 400 : 20 : 1 (equivalent concentration of supported catalyst: 1.5 mM) in 1 ml CH_2Cl_2, 2 h at 20 °C under an argon atmosphere. Product analysis as described in Table 1.

increase in total oxidation yield was accompanied by a marked increase in the ratio of alcohol to ketone, this ratio reaching 10, a remarkable value for an oxidation catalysed by a Mn–porphyrin, in the case of heptane.

We have already reported that the SiO_2-supported Mn(tmpyp)Cl catalyst led to higher yields of hydroxylation of poorly reactive linear alkanes with markedly higher ratios of alcohol to ketone than the corresponding homogeneous Mn–porphyrin catalysts.[2] This tendency is even more pronounced with ClaypMn (*ca.* 50% yield for heptane). In order to know whether the different environments of the Mn catalyst in ClaypMn and in SiO_2pMn could change the substrate specificity in favour of linear alkanes, competition experiments were performed on alkane mixtures (in fact pentane–alkane 2 : 1 mixtures). As shown in Table 2, the ratio between the oxidation products derived from pentane and those derived from either adamantane, cyclo-octane, or heptane were always higher with ClaypMn than with SiO_2pMn. The largest difference was observed for competitions between pentane and adamantane as the ratio obtained with ClaypMn was seven times more in favour of pentane than with SiO_2pMn. Actually, pentane was found to be much less reactive than adamantane in oxidations catalysed by SiO_2pMn or soluble Mn(tmpyp)Cl (relative reactivity ratio of 0.05 : 1 with both catalysts under the conditions used), but only three times less reactive in oxidations catalysed by ClaypMn (ratio of 0.35 : 1). This difference between ClaypMn and SiO_2pMn was much lower for competitions between pentane and heptane, suggesting that it was related to a particular ability of ClaypMn to oxidize small and not bulky alkanes. Further experiments are required to characterize the mode of binding of Mn(tmpyp) to montmorillonite and to understand its substrate specificity.

The ClaypMn catalyst, which is very easily prepared in one step from commercially available compounds and easily recovered by simple filtration at the end of the reactions, presents two main advantages when compared with homogeneous or silica-supported Mn–porphyrin catalysts. It can be used in a wide variety of solvents including CH_3OH and H_2O, and it exhibits a particular ability to oxidize poorly reactive short linear alkanes.

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