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Supported polyhalogenated metalloporphyrins as catalysts for the oxidation of cycloalkanes with molecular oxygen in Lyons system

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Abstract

The synthesis and catalytic activity of the polyfluorinated manganese, iron and cobalt porphyrins in homogeneous reaction and of these metallocomplexes supported on functionalized silica gel, polystyrene and montmorillonite K10 have been studied in oxidation of cyclooctane with molecular oxygen (as air) to cyclooctanone and cyclooctanol without the use of sacrificial co-reductant.

The supported cobalt porphyrin is more active than the supported iron and manganese porphyrins and the activity of supported cobalt porphyrin is similar for all the supports. We have found that the silica as the support has reversed the order of activity of the supported catalysts in comparison to the metalloporphyrins in homogeneous system. The kind of support determines the product yields and the selectivity to cyclooctanone and cyclooctanol. We have also shown that the supported catalysts can be recycled and re-used.

Keywords: Metalloporphyrins; Supported metalloporphyrins; Hydrocarbon oxidation; Cyclooctane

1. Introduction

Selective catalytic oxidation of hydrocarbons with molecular oxygen and metalloporphyrins as catalysts in Lyons system is one of the most attractive transformations in organic synthesis [1–9]. It is evident that the use of molecular oxygen (as air) which is an inexpensive, abundant and readily available oxidant in place of oxygen donors is clearly desirable on economic and environmental grounds. The main drawbacks for practical use of these catalysts is the deactivation by irreversible dimerization and the oxidative self-destruction of metalloporphyrins. There are two ways to circumvent these problems. The first one is extensive halogenation of the metalloporphyrins with electron withdrawing substituents on the porphyrin macrocycle. These complexes are known as efficient catalysts for the direct reaction of hydrocarbons with molecular oxygen at unprecedented rates [10,11].

The second way is immobilization of metalloporphyrins by binding them to the solid supports [12–17]. In this study we have applied the combination of electron withdrawing substituted metalloporphyrins with immobilization on inorganic or organic supports. It may prevent molecular aggregation and other destructive reactions of catalysts under oxidizing conditions. Finally, the immobilization of metalloporphyrins offers several practical advantages over soluble catalysts such as facilitation of catalyst separation from the reaction mixture, simplification of procedures for catalyst recycling and the possible adaptation of the immobilized catalyst for continuous flow processes.

In our previous papers [7,8], we have described how the change of the axial ligand or/and substituents of the metalloporphyrin complex can considerably enhance the catalytic activity of these catalysts in the oxidation of the cycloalkanes with molecular oxygen.

In this work, we will continue our study on the application of supported metalloporphyrins (Fig. 1) in the oxidation of cyclooctane with molecular dioxygen (as air) and in the absence of a reducing agent because there is only scarce information concerning the direct oxidation of hydrocarbons with molecular oxygen in the presence of supported metalloporphyrins as catalysts in Lyons system [9]. The activity of such catalysts appears to be dependent on the character of the metal center and the kind of the support. We have found that the supported catalysts can be recycled and re-used.

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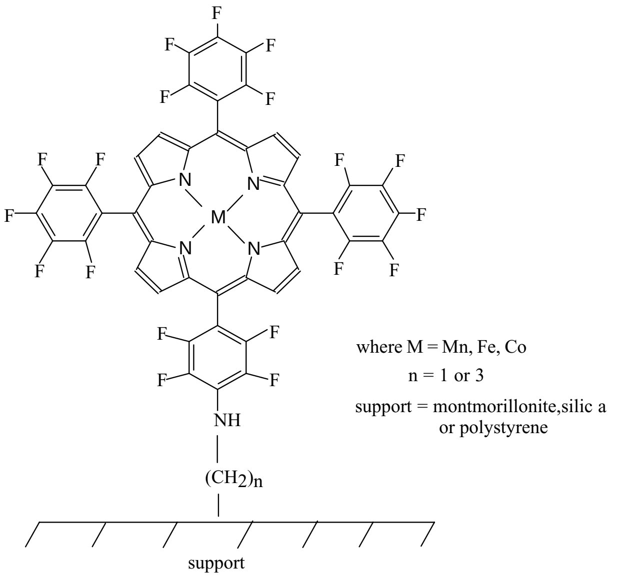

Fig. 1. Structures of the investigated supported metalloporphyrins.

2. Experimental

The catalytic oxidation of cyclooctane has been carried out in a stainless steel batch reactor system at the optimum temperature of 120 °C and under the air pressure of 10 bars, with the molar ratio of cyclooctane to oxygen set at 6.5. A Teflon liner reactor of 1 L volume equipped with magnetic stirrer was used.

In the typical experiment, the catalyst having the concentration of 3.3×10^{-4} M of metalloporphyrin or its equivalent for the supported metallocomplexes was introduced into the reaction mixture when the required reaction conditions were attained. After 6 h of reaction time the oxidation was stopped by immersing the hot reactor in a cold water bath. The products were analyzed by means of an Agilent Technologies 6890 N gas chromatograph equipped with an Innovax (30 m) column. The pentafluorotetraphenylporphyrin ligand (TPFPP) was synthesized by the procedure used by Lindsay et al. [18]. The manganese, iron and cobalt complexes were prepared by DMF metalation procedure [19]. The supported catalysts were synthesized according to the procedure previously described [20] from 3-aminopropyl-functionalized silica gel (Fluka), aminomethylpolystyrene (Fluka), 3-amino propylmontmorillonite and metalloporphyrins. Metalloporphyrins and ligands were purified by successive chromatography on silica gel or alumina columns. The purity of the ligands and metalloporphyrins were checked by UV-Vis, IR and mass spectroscopy.

The amount of metalloporphyrins on the supports were determined by elemental analysis and by UV-Vis spectroscopy of the solution left after impregnation.

Electronic spectra of the supported metalloporphyrins were obtained in nujol mull between quartz plates.

3. Results and discussion

The presence of metalloporphyrins on the supports was confirmed by the UV-Vis spectroscopy for all the studied metalloporphyrin-supported catalysts. Typical spectra for manganese porphyrin in solution and manganese, iron and cobalt complexes deposited on montmorillonite K10 are shown in Fig. 2. In the dichloromethane solution of the Mn(TPFPP)Cl (Fig. 2a) a Soret band is visible at 474 nm. After immobilization of Mn(TPFPP)Cl on montmorillonite K10 no significant changes in the Soret band position was observed in the UV-Vis spectrum (Fig. 2b), indicating that the porphyrin ring was not modified during the anchoring procedure. For the other two metalloporphyrins Fe(TPFPP)Cl and Co(TPFPP)Cl (Fig. 2c and d) we have observed a small redshift of the Soret bands from 411 to 422 nm for the iron complex and from 423 to 435 nm for the cobalt compound. The UV-Vis spectra of the supported metalloporphyrins and metalloporphyrins in homogenous phase are almost identical which indicates that the macrocyclic complex is retained after deposition on the support. Also UV-Vis spectra of metalloporphyrins supported on polystyrene and silica gel show similar small changes of the Soret band like in the case of metallocomplexes on montmorillonite K10. This proves that the porphyrin ring was not modified during the metallocomplex impregnation.

We have investigated the oxidation reaction of cyclooctane with polyhalogenated metalloporphyrins Mn(TPFPP)Cl, Fe(TPFPP)Cl, Co(TPFPP)Cl and with the same complexes covalently bound to 3-aminopropylmontmorillonite, aminopropylsilica and 3-amino methylpolystyrene without adding the sacrificial co-reductant. In all the cases the only products observed were cyclooctanone and cyclooctanol. All the polyhalogenated metalloporphyrins and supported polyhalogenated metalloporphyrins were found to be active catalysts for cyclooctane oxidation. A summary of results can be found in Table 1. For the liquid phase metalloporphyrins, the most active was the manganese complex showing the highest yields whereas bound to silica gel turned out to be

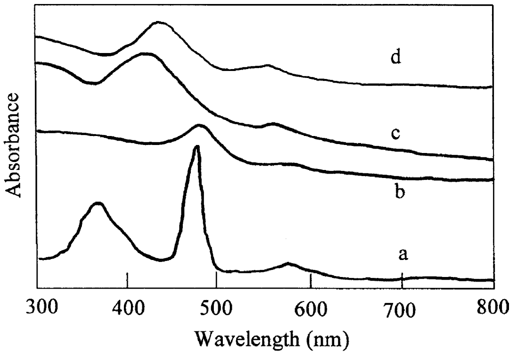

Fig. 2. UV-Vis spectra at room temperature: (a) dichloromethane solution of Mn(TPFPP)Cl, (b) in nujol mull Mn(TPFPP)Cl on montmorillonite K10, (c) in nujol mull Fe(TPFPP)Cl on montmorillonite K10, (d) in nujol mull Co(TPFPP)Cl on montmorillonite K10.

Table 1
Oxidation of cyclooctane catalyzed by different metalloporphyrins in homogeneous system and supported on silica, polystyrene and montmorillonite K10

Catalyst	Cyclooctanone yield, TON[a]	Cyclooctanol yield, TON	C-one/C-ol ratio	Loading of porphyrin (%, w/w)
MnTPFPPCl	37862	7084	5.3	–
FeTPFPPCl	27060	3740	7.2	–
CoTPFPPCl	22660	4180	5.4	–
MnTPFPP/SiO_2	2640	440	6.0	5.5
FeTPFPP/SiO_2	9680	1320	7.3	8.7
CoTPFPP/SiO_2	16720	3740	4.5	7.1
MnTPFPP/PS	5720	880	6.5	2.2
FeTPFPP/PS	6160	880	7.0	2.7
CoTPFPP/PS	15620	3300	4.7	2.0
MnTPFPP/M-K10	11440	1760	6.5	1.9
FeTPFPP/M-K10	6380	880	7.3	2.2
CoTPFPP/M-K10	16720	3520	4.8	2.1
CoTPFPP/M-K10[b]	18480	1980	9.4	7.1

Conditions as in text.

[a] Mol product × mol per catalyst × h^{-1}.

[b] The second run.

the least efficient catalyst. It is interesting to note that after attachment of polyfluorinated metallocomplexes to silica gel, we have observed the inversion of the order of activity of the metalloporphyrins (Fig. 3). The most active on silica gel was cobalt porphyrin Co(TPFPP)Cl catalyst.

The second catalyst series we have studied was polyfluorinated metalloporphyrins bound to the surface of polystyrene (PS). For the supported catalysts MnTPFPP/PS and FeTPFPP/PS only small amounts of oxygenated products were detected and the activity of these catalysts was relatively low. Manganese and iron metalloporphyrins deposited on montmorillonite also showed relatively low activity. Only cobalt complex deposited on both polystyrene and montmorillonite as support gave good yields. It appeared to be stable under oxidation conditions and it is possible to re-use this catalyst with very similar ketone and alcohol yields and even with better selectivity as shown by the example of this complex supported on montmorillonite (Table 1). The selectivities and the yields of products presented in Table 1 were only in case of supported cobalt porphyrins comparable to the results obtained for homogeneous catalysts. It is interesting to notice that for supported cobalt metalloporphyrins as catalysts the yields of the products are independent of the kind of support. All these supported catalysts were found to be the efficient catalysts for the hydroxylation of cyclohexane and heptane and for epoxidation of cyclooctane with iodosobenzene as oxygen atom donor [20]. It is not clear why the chosen supports have changed the catalytic properties of metalloporphyrins in our system but the same effect was observed in oxidation reactions of isobutane with supported metalloporphyrins as catalysts in Lyons system [9].

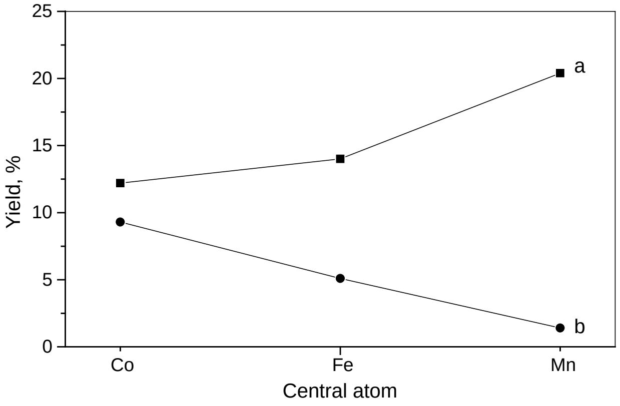

Fig. 3. Yield of products for different metals: (a) in homogeneous system, (b) supported on silica.

All the supported catalysts have shown a lower catalytic activity in comparison with homogeneous systems. We suggest that this is due to a less restricted access for reagents to the metal center in the homogeneous catalysis as compared to the heterogeneous one which could be caused by a different position of the macrocyclic ring. In the case of heterogeneous catalyst, the porphyrin ring is positioned perpendicularly to the surface of the support making the access to the catalytic center more difficult.

Further studies are necessary to compare the results obtained in our system with the systems where the metalloporphyrin ring is bound parallel to the support surface.

4. Conclusions

The catalytic results show that the activity of supported catalysts seems to be dependent on the character of the metal center and the kind of the support. It was demonstrated that the choice of the support influences the yields of the products: cyclooctanone and cyclooctanol and the selectivity. These results are also valuable because they indicate that supported metalloporphyrin oxidation catalysts can be used in flow reactions which utilize dioxygen as the oxidant and in which the sacrificial co-reductants are not required. All the supported metalloporphyrins used in these processes may be readily prepared.

Acknowledgements

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