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A Ruthenium Porphyrin Catalyst Immobilized in a Highly Cross-linked Polymer

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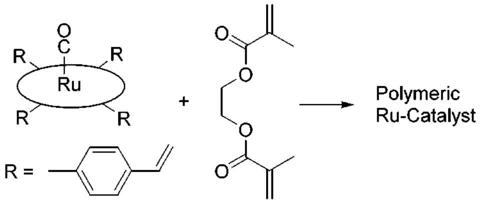
ABSTRACT



An immobilized Ru(*meso*-tetraarylporphyrin) complex was shown to be a very efficient catalyst for the epoxidation of olefins. In the presence of HBr, alcohols and even alkanes could be converted to the corresponding ketones. For the latter reactions the polymeric catalyst displayed a significantly enhanced activity when compared to that of the homogeneous version.

Macroporous, highly cross-linked polymers are excellent matrices for immobilized transition metal catalysts. As a result of the permanent pore structure and the high surface area (typically between 100 and 600 m^2 g^{-1}),[1] the accessibility of the catalytically active centers is very good. Furthermore, a variety of different solvents can be used for catalysis, whereas for classical Merrifield-type resins solvents with good swelling abilities are needed. An additional advantage is that the catalysts are fixed within a very rigid matrix. As a result, catalyst deactivation by intermolecular reactions is strongly suppressed. Moreover, the microenvironment of the catalyst and thus the activity and selectivity can be modified using the technique of molecular imprinting.[2] Given these advantages, it is surprising that polymeric supports of this kind have rarely been employed compared to other organic matrices.[3,4]

Mimicking natural metalloenzymes, manganese- and iron-containing porphyrin catalysts have mainly been used for oxidation reactions, but in recent years Ru(CO)(porphyrin) complexes have received increasing attention.[5] With 2,6-disubstituted pyridine *N*-oxides as the oxidant, the efficient conversion of olefins and sulfides to epoxides and sulfoxides is possible. In the presence of mineral acids even inactivated alkanes can be oxidized.

Immobilized ruthenium porphyrin catalysts for alkene epoxidation have been prepared by Che et al. They have employed a standard Merrifield resin with covalently attached Ru-porphyrins[6] or a surface modified mesoporous molecular sieve with coordinative bonding to a Ru-porphyrin.[7] In both

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(1) Santora, B. P.; Gagné, M. R.; Moloy, K. G.; Radu, N. S. *Macromolecules* **2001**, *34*, 658−661.

(2) *Molecularly Imprinted Polymers*; Sellergren, B, Ed.; Elsevier: Amsterdam, 2001.

(3) For some selected examples see: (a) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, *57*, 4637−4662 and references therein. (b) Taylor, R. A.; Santora, B. P.; Gagné, M. R. *Org. Lett.* **2000**, *2*, 1781−1783. (c) Canali, L.; Cowan, E.; Deleuze, H.; Gibson, C. L.; Sherrington, D. C. *Chem. Commun.* **1998**, 2561−2562. (d) Nozaki, K.; Itoi, Y.; Shibahara, F.; Shirakawa, E.; Ohta, T.; Takaya, H.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 4051−4052. (e) Breysse, E.; Pinel, C.; Lemaire, M. *Tetrahedron: Asymmetry* **1998**, *9*, 897−900. (f) Santora, B. P.; Larsen, A. O.; Gagné, M. R. *Organometallics* **1998**, *17*, 3138−3140. (g) Salvadori, P.; Pini, D.; Petri, A. *J. Am. Chem. Soc.* **1997**, *119*, 6929−6930.

(4) For molecularly imprinted polymers with transition metal catalysts see: (a) Polborn, K.; Severin, K. *Chem. Eur. J.* **2000**, *6*, 4604−4611. (b) Polborn, K.; Severin, K. *Eur. J. Inorg. Chem.* **2000**, 1687−1692. (c) Polborn, K.; Severin, K. *Chem. Commun.* **1999**, 2481−2482. (d) Locatelli, F.; Gamez, P.; Lemaire, M. *J. Mol. Catal. A* **1998**, *135*, 89−98. (e) Matsui, J.; Nicholls, I. A.; Karube, I.; Mosbach, K. *J. Org. Chem.* **1996**, *61*, 5414−5417.

(5) (a) Gross, Z.; Ini, S. *Inorg. Chem.* **1999**, *38*, 1446−1449. (b) Liu, C.-J., Yu, W.-Y.; Che, C.-M.; Yeung, C.-H. *J. Org. Chem.* **1999**, *64*, 7365−7374. (c) Ohtake, H.; Higushi, T.; Hirobe, M. *Heterocycles* **1995**, *40*, 867−903 and references therein.

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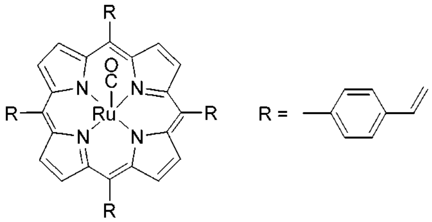
cases selective catalysts with good activities were obtained. For the latter system, however, catalyst leaching and/or deactivation was found to be a problem.

Here we describe an immobilized ruthenium porphyrin catalyst, the basic matrix of which is a highly cross-linked organic polymer. With this catalyst we able to efficiently oxidize olefins, secondary alcohols, and surprisingly even alkanes. Especially in the latter reactions the heterogeneous catalyst was clearly superior to the corresponding homogeneous version.

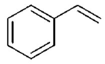
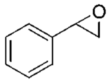
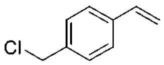
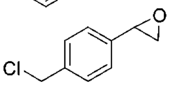
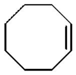
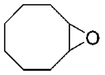
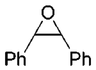
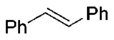
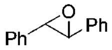
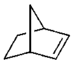
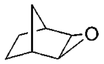
To incorporate the ruthenium complex, we first synthesized the vinyl-substituted *meso*-tetraarylporphyrin complex **1** by reaction of the free base porphyrin[8] with [Ru$_3$(CO)$_{12}$] in boiling toluene. It is important to add a scavenger such as styrene to the reaction mixture. Otherwise the vinyl groups of the porphyrin are partially reduced, presumably in a ruthenium-catalyzed reaction.



1

Complex **1** was subsequently copolymerized with ethylene glycol dimethacrylate (**1**:EGDMA = 1:99) in the presence of an equal volume of CHCl$_3$/THF (98:2), which acts as a porogen. To initiate the reaction we employed 2,2′-azobis-(4-methoxy-2,4-dimethylvaleronitrile). The dark red polymer **P1** was ground and sieved (particle size, 25−100 μm). The nearly quantitative incorporation of the Ru-complex in the polymer was evidenced by the fact that the THF washing solutions were colorless and by ICP analysis.

Table 1. Catalytic Epoxidation of Olefins with the Polymeric Catalyst **P1**[a]

substrate	product	conversion [%]
		> 99
		93
		94
		93
		26
		96

[a] The reactions were performed in CHCl$_3$ at room temperature with a substrate/Cl$_2$pyNO/catalyst molar ratio of 500:750:1. The conversion was determined after 24 h by gas chromatography or ^{1}H NMR spectroscopy.

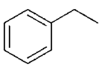
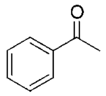
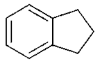
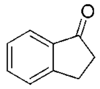
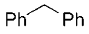
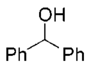
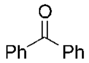
To evaluate the catalytic properties of our polymer we first investigated the epoxidation of various olefins. The reactions were performed with 2,6-dichloropyridine *N*-oxide as the oxidant. By using only 0.2 mol % catalyst excellent yields of the corresponding epoxides were obtained after 24 h, the only exception being *trans*-stilbene (Table 1). This substrate is known to be less suited for Ru(porphyrin)-catalyzed epoxidations.[9] A competition experiment with the catalyst **P1** and equal amounts of *cis*- and *trans*-stilbene gave 93% *cis*- and 31% *trans*-stilbeneoxide. This is in contrast to the results obtained with the homogeneous catalyst **1** (94% *cis*; 5% *trans*), indicating that the selectivity is affected by the polymeric support. Interestingly, an increased reactivity toward *trans*-stilbene was also observed for the resin-bound catalyst described by Che.[6]

Overall the activity of the polymeric catalyst **P1** in epoxidation reactions is comparable or slightly higher than that of the homogeneous version **1**: for styrene an initial turnover frequency of 40 h^{-1} was determined; 27 h^{-1} was found for catalyst **1**. The stability of the catalyst **P1** is good: using larger amounts of styrene, turnover numbers of more than 5×10^3 have been observed. Nevertheless, a slightly decreased activity (approximately 15%) was found upon recycling of the catalyst by filtration.

It has been shown by Hirobe et al. that in the presence of HCl and HBr, Ru(porphyrin) complexes can be used to oxidize compounds with very low reactivity such as alkanes.[5] The utilization of supported catalysts for this type of reaction is especially challenging because the substrate will have to compete with a very high local concentration of a polymeric matrix having a similar reactivity (autoxidation). Consequently, alkane oxidations with immobilized Ru(porphyrin) complexes have not been described so far.

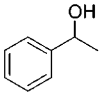
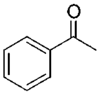
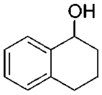
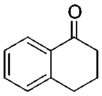
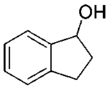
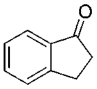
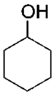
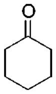
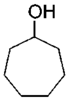
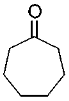
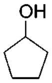
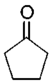
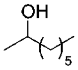
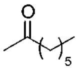
With 1 mol % of the polymeric catalyst **P1**, however, aromatic alkanes such as ethylbenzene or Indane are oxidized to acetophenone and indanone in good or excellent yields (Table 2). Here, the difference between **P1** and the homogeneous catalyst **1** is striking, particularly for the oxidation

Table 2. Catalytic Oxidation of Aromatic Alkanes[a]

substrate	product	cat. = **1** conv. [%]	cat. = **P1** conv. [%]
		2	74
		47	>99
		5	35
		52	64

[a] The reactions were performed in a solution of HBr in benzene at 55 °C with a substrate/Cl$_2$pyNO/catalyst molar ratio of 100:150:1. The conversion was determined after 24 h by gas chromatography.

Table 3. Catalytic Oxidation of Secondary Alcohols[a]

substrate	product	time [h]	cat. = **1** conv. [%]	cat. = **P1** conv. [%]
		1	1	>99
		1	7	>99
		2	91	>99
		2	45	98
		2	20	>99
		3	22	90
		3	99	96

[a] The reactions were performed in a solution of HBr in benzene at 55 °C with a substrate/Cl_2pyNO/catalyst molar ratio of 100:150:1. The conversion was determined after the times given by gas chromatography or ^{1}H NMR spectroscopy.

of ethylbenzene: only small amounts of acetophenone are found in reactions with the homogeneous catalyst **1**. Plausible intermediates for this type of reaction are alcohols. In the case of diphenylmethane, this intermediate can be detected in the reaction mixture.

The results described above prompted us to investigate the catalytic oxidation of secondary alcohols.[10] By using different aromatic and aliphatic (cyclic and linear) substrates, Cl_2pyNO as the oxidant, and 1 mol % **P1** as the catalyst, the corresponding ketones were obtained in mostly quantitative yields in less than 3 h (Table 3). Again, significantly lower yields were obtained with the homogeneous catalyst **1**. In some cases the initial turnover frequencies differ by more than 1 order of magnitude!

The results described above highlight the potential of highly cross-linked polymers as supports for site-isolated[11] porphyrin catalysts. Because the complex is fixed in a very rigid matrix, destructive autoxidation of the catalyst and the support is reduced. This is of special significance if low reactivity substrates such as alkanes are employed.

Currently, we are investigating whether the selectivity of polymeric catalysts such as **P1** can be manipulated in a controlled fashion using the technique of molecular imprinting.

Supporting Information Available: Methods for the preparation of the ruthenium complex **1** and the polymer **P1** together with spectroscopic and physical data (^{1}H and ^{13}C NMR, IR, elemental analysis, apparent dry density, swelling) and detailed procedures for the catalytic oxidations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Yu, X.-Q.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2000**, *122*, 5337−5342.

(7) (a) Liu, C.-J.; Yu, W.-Y.; Li, S.-G.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 7364−7369. (b) Liu, C.-J.; Li, S.-G.; Pang, W.-Q.; Che, C.-M. *Chem. Commun.* **1997**, 65−66.

(8) The porphyrin was synthesized from pyrrole and *p*-vinyl-benzaldehyde following a standard procedure: Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476−477.

(9) (a) Berkessel, A.; Frauenkorn, M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2265−2266. (b) Ohtake, H.; Higuchi, T.; Hirobe, M. *Tetrahedon Lett.* **1992**, *33*, 2521−2524.

(10) For the catalytic oxidation of alcohols with Ru(porphyrin) complexes see: (a) Gross, Z.; Ini, S. *Org. Lett.* **1999**, *1*, 2077−2080. (b) Ohtake, H.; Higuchi, T.; Hirobe, M. *J. Am. Chem. Soc.* **1992**, *114*, 10660−10662.

(11) For site-isolated cobalt complexes within a cross-linked polymer see: (a) Padden, K. M.; Krebs, J. F.; MacBeth, C. E.; Scarrow, R. C.; Borovik, A. S. *J. Am. Chem. Soc.* **2001**, *123*, 1072−1079. (b) Sharma, A. C.; Borovik, A. S. *J. Am. Chem. Soc.* **2000**, *122*, 8946−8955.