This article was downloaded by: [University of California, San Francisco] On: 10 December 2014, At: 04:45 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

MANGANESE(III) PORPHYRIN SUPPORTED ON POLYSTYRENE AS A HETEROGENEOUS ALKENE EPOXIDATION AND ALKANE HYDROXYLATION CATALYST

S. Tangestaninejad^a, M. H. Habibi^a, V. Mirkhani^a & M. Moghadam^a ^a Department of Chemistry, Isfahan University, Isfahan, 81744, Iran Published online: 16 Aug 2006.

To cite this article: S. Tangestaninejad, M. H. Habibi, V. Mirkhani & M. Moghadam (2002) MANGANESE(III) PORPHYRIN SUPPORTED ON POLYSTYRENE AS A HETEROGENEOUS ALKENE EPOXIDATION AND ALKANE HYDROXYLATION CATALYST, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:21, 3331-3337, DOI: 10.1081/SCC-120014040

To link to this article: http://dx.doi.org/10.1081/SCC-120014040

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

SYNTHETIC COMMUNICATIONS Vol. 32, No. 21, pp. 3331–3337, 2002

MANGANESE(III) PORPHYRIN SUPPORTED ON POLYSTYRENE AS A HETEROGENEOUS ALKENE EPOXIDATION AND ALKANE HYDROXYLATION CATALYST

S. Tangestaninejad,^{*} M. H. Habibi, V. Mirkhani, and M. Moghadam

Department of Chemistry, Isfahan University, Isfahan 81744, Iran

ABSTRACT

Carboxymethylated crosslinked polystyrene resin [poly(4styrylmethylacylchloride) (PSA)] support have been used to covalently attach manganese(III) tetrakis(4-aminophenyl)porphyrin. This catalyst was found to be efficient for alkene epoxidation and alkane hydroxylation by sodium periodate. This new hydrogenised catalyst is of high stability and reusability.

The use of synthetic metalloporphyrins as catalysts for hydrocarbons oxidation has received much attention over the last two decades.^[1–3] To date, however, the utility of these metalloporphyrin catalysts in synthesis has been limited due to catalyst deactivation through self-destruction and

3331

DOI: 10.1081/SCC-120014040 Copyright © 2002 by Marcel Dekker, Inc. 0039-7911 (Print); 1532-2432 (Online) www.dekker.com

^{*}Corresponding author. E-mail: stanges@sci.ui.ac.ir

3332

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

TANGESTANINEJAD ET AL.

difficulty in recovery of the expensive catalyst. Heterogeneous analogues of these catalysts not only simplify their use and facilitate product separation, and prevent intramolecular self-oxidation, but also offer a considerable economic benefit if the catalyst recycled and reused.^[4]

Different methods have been employed to immobilize metalloporphyrins on organic or inorganic supports.^[5-15] However, attachment of metalloporphyrins to some of these supports is a reversible process, therefore, leaching and loss of their catalytic activities remains a problem. We now report a novel heterogeneous catalyst for hydrocarbon mono-oxygenation based on chemically modified cross-linked chloromethylated polystyrene. The manganese(III) porphyrin strongly bounds to the support forming a robust, reusable and active catalyst for oxidation of alkenes and alkanes.

Modified polystyrene support was obtained by cyanation of chloromethylated polystyrene in dimethylsulfoxide (DMSO) and hydrolysis to carboxylic acid by a slight modification of the previously reported method by Sherrington (Sch. 1).^[16] The reaction of this carboxymethylated polystyrene with thionyl chloride afforded a solid support, which can be considered as an insoluble benzoyl chloride. This polymer could readily react with compounds bearing appropriate functional groups such as amines. Manganese(III) tetrakis(4-aminophenyl)porphyrin could be covalently attached to this support in DMF. The polymer-bound porphyrin is insoluble in common organic solvents. The reflectance spectrum clearly indicates a Soret band at 466 nm and a Q band at 566 nm. IR spectrum of the solid supported manganese porphyrin shows a ν (CO) at 1670 cm⁻¹. The degree of manganese porphyrin incorporation into the polymer was determined by neutron activation analysis (NAA), which shows a value of about 4.5% w/w. The covalent bonding of the polymer and metalloporphyrin is so strong that manganese porphyrin is not eluted from the polymer with water and common organic solvents.

Preliminary investigation on epoxidation of cyclooctene as a typical substrate in the presence of Mn(TNH₂PP)-PSA by sodium periodate revealed



©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

MANGANESE(III) PORPHYRIN

3333

high activity of the catalyst in 2:1 CH₃CN/H₂O mixture. The effect of different axial ligands upon the rate of epoxidation of cyclooctene was also investigated. The epoxidation rate decreased in the following order: imidazole > t-butylpyridine > 1-methylimidazole > pyridine. The optimum condition used for the epoxidation of cyclooctene with this catalyst, employed the catalyst: oxidant: substrate: imidazole in molar ratio 1:100:50:10.

Mn(TNH₂PP)-PSA is an efficient catalyst for epoxidation of different alkenes and the epoxide yields (Table 1) are comparable to those obtained using homogeneous catalysts.^[17–19] In the case of stilbenes, the *trans*-stilbene was converted to trans-epoxide in 55% yield, but cis-stilbene afforded a 75:10 mixture of *cis*- and *trans*-epoxides. Epoxidation of R-(+)-limonene gave a mixture of 1,2- and 8,9-epoxides. The ratio among 1,2- and 8,9-epoxides was found to be 1.25:1.

The catalytic hydroxylation of alkanes and arylalkanes with sodium periodate was performed in the presence of Mn(TNH₂PP)-PSA under the same conditions described for alkene epoxidation (Table 2).

To assess long-term stability and reusability of Mn(TNH₂PP)-PSA, styrene was used as a model substrate, and recycling experiments were carried out with a single sample of the catalyst. After each experiment, the catalyst was removed by simple filtration, washed with water and acetonitrile and reused. The resulted yields and leaching data obtained are listed in Table 3.

We have shown that polystyrene-bound manganese(III) tetrakis(4aminophenyl)porphyrin can be used as an effective catalyst for alkene epoxidation and alkane hydroxylation reactions. The catalyst is robust toward destructive reactions and can be easily recovered by simple filtration at the end of the reactions.

EXPERIMENTAL

The porphyrin ligand, 5,10,15,20-tetrakis(4-aminophenyl) porphyrin, was prepared and metallated according to the literature procedures.^[20,21] Alkenes and alkanes were obtained from Merck or Fluka and were passed through a column containing active alumina to remove peroxidic impurities.

Modification of Chloromethylated Polystyrene for Preparation of Poly(4-styrylmethyl)acylchloride

To a solution of DMSO (50 mL), were added chloromethylated polystyrene (5g), sodium cyanide (5g) and refluxed for 4h. After cooling, the polymer was filtered, washed with water and acetone and dried at 60° C.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

3334

d

TANGESTANINEJAD ET AL.

Table 1.	Epoxidation of	of Alkenes with	1 NaIO ₄ Cata	alyzed by	Mn(TNH ₂ I	PP)-PSA in
the Presen	ce of Imidazol	e at Room Te	mperature			

Entry	Alkene	Conversion (%) ^a	Epoxide Yield (%) ^a	Reaction Time (h)
1	\bigcirc	91	91	7
2	\bigcirc	88	68	7
3	\bigcirc	100	85	3
4		100	70	2
5	Å	80	80	7
6	$\sim\sim\sim$	65	65	7
7		75	75	7
8	$\sum_{i=1}^{n}$	70	39(1,2-Epoxide) ^b 31(8,9-Epoxide) ^b	7
9		55	55(trans-Epoxide) ^b	7
10		85	75(cis-Epoxide) ^b 10(trans-Epoxide) ^b	7

^aGLC yield based on starting alkene.

^bBoth ¹H NMR and GLC data approved the reported yields.

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

MANGANESE(III) PORPHYRIN

3335

Table 2.	Hydroxylation	of Alkanes with	NaIO ₄ Catalyzed	by Mn(TNH ₂ PP)-PS	4
in Presenc	e of Imidazole a	at Room Temper	rature		

Entry	Alkane	Ketone (%) ^a	Alcohol (%) ^a	Reaction Time (h)
1	\bigcirc	33	17	8
2	\bigcirc	40	_	8
3	F	35	19	8
4	\bigcirc	70	_	8
5		35	_	8
6		-	43	8
7		29	_	8
8		60	_	8

^aGLC yield based on starting alkane.

Table 3. The Result of $Mn(TNH_2PP)$ -PSA Catalyst Recovery and the Manganese Leached in the Epoxidation of Styrene with Sodium Periodate

Run	Conversion (%) ^a	Mn Leached (%) ^b	Time (h)
1	100	1	3
2	95	0.7	3
3	92	0	3
4	92	0	3

^aGLC yield based on starting styrene.

^bMeasured by atomic absorption spectrometry and based on initial manganese concentration.

YY.

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

TANGESTANINEJAD ET AL.

This polymer was heated at 50° C for 4 h in concentrated sulfuric acid (100 mL) for hydrolysis of the cyanide groups.

The polymer was filtered, washed several times with water and dried. The polymer was refluxed in thionyl chloride (20 mL) for 8 h. After cooling to room temperature, the thionyl chloride was removed under reduced pressure and the resulted carboxymethylated polystyrene was washed with acetone and dried.

The FT-IR spectra of polymer 2–4 showed characteristic bands due to $C\equiv N$ and C=O stretching vibrations at 2212, 1765 and 1705 cm⁻¹, respectively. The conversion yield of first step of the reactions shown in Sch. 1, determined potentiometrically by measuring of the released chloride ion, was 80–85%. The conversions of the second and third steps, determined from the IR spectra, were almost complete.

Immobilization of Mn(TNH₂PP) on Poly(4-styrylmethylacylchloride)

To a solution of $Mn(TNH_2PP)$ (0.5 g) in DMF (50 mL), were added poly(4-styrylmethylacylchloride) (5 g) and triethylamine (3 mL). The mixture was heated at 100°C for 8 h. After cooling to room temperature, the catalyst was filtered, washed with methanol and acetone and dried.

Typical Procedure for Oxidation Reactions Catalyzed by Mn(TNH₂PP)-PSA

All of the reactions were carried out at room temperature under air in a 25 mL flask equipped with a magnetic stirrer bar. A solution of NaIO₄ (2 mmol) in H₂O (5 mL) was added to a mixture of alkene or alkane (1 mmol), Mn(TNH₂PP)-PSA (20 µmol) and imidazole (0.2 mmol) in CH₃CN (10 mL). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH₂Cl₂ (20 mL) and filtered. The resin was thoroughly washed with CH₂Cl₂ an combined washings and filterates were purified on silica-gel plates or silica-gel column. IR and ¹H NMR spectral data confirmed the identities of the products.

ACKNOWLEDGMENT

We thank the financial support of this work by the Isfahan University Research Council.

3336

©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.

MANGANESE(III) PORPHYRIN

3337

REFERENCES

- 1. Meunier, B. Chem. Rev. 1992, 92, 1411.
- 2. Mansuy, D. Coord. Chem. Rev. 1993, 125, 129.
- Sono, M.; Roach, M.P.; Coulter, E.D.; Dawson, J.H. Chem. Rev. 1996, 96, 2841.
- 4. Sherrington, D.C. Catalysis Today 2000, 57, 87.
- 5. Sacco, H.C.; Iamamoto, Y.; Lindsay Smith, J.R. J. Chem. Soc., Perkin Trans. 2 2001, 181.
- Yu, X.-Q.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. J. Am. Chem. Soc. 2000, 122, 5337.
- 7. Campestrini, S.; Meunier, B. Inorg. Chem. 1992, 31, 1999.
- Iamamoto, Y.; Ciuffi, K.J.; Sacco, H.C.; Prado, M.C.; Moraes, M.; Nascimento, O.R. J. Mol. Catal. 1994, 88, 167.
- 9. Geier, G.R.; Sasaki, T. Tetrahedron 1999, 55, 1859.
- Battioni, P.; Bartoli, J.F.; Mansuy, D.; Byun, Y.S.; Traylor, T.G. J. Chem. Soc., Chem. Commun. 1992, 1051.
- 11. Tangestaninejad, S.; Mirkhani, V. J. Chem. Res. (S). 1998, 788.
- 12. Tangestaninejad, S.; Moghadam, M. Synth. Commun. 1998, 28, 427.
- 13. Gitzel, J.; Ohno, H.; Tsuchida, E.; Woehrle, D. Polymer 1986, 27, 1781.
- Yu, X.-Q.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. J. Am. Chem. Soc. 2000, 122, 5337.
- 15. Woehrle, D.; Gitzel, J. Makromol. Chem., Rapid Commun. 1988, 9, 229.
- 16. Ma, J.; Sherrington, D.C. J. Chem. Res. (S) 1995, 119.
- 17. Mohajer, D.; Tangestaninejad, S. J. Chem. Soc., Chem. Commun. 1993, 240.
- 18. Mohajer, D.; Tangestaninejad, S. Tetrahedron Lett. 1994, 35, 945.
- 19. Mohajer, D.; Tayebee, R.; Goudarziafshar, H. J. Chem. Res. (S) 1999, 168.
- 20. Semeikin, A.S.; Koifman, O.I.; Berezin, B.D.; Khim. Geterotsikl. Soed. **1982**, *10*, 1354.
- Adler, A.D.; Longo, F.R.; Kampas, F.; Kim, J. J. Inorg. Nucl. Chem. 1970, 32, 2443.

Received in Japan August 7, 2001



©2002 Marcel Dekker, Inc. All rights reserved. This material may not be used or reproduced in any form without the express written permission of Marcel Dekker, Inc.