

Epoxidation of alkenes with NaIO_4 catalyzed by an efficient and reusable natural polymer-supported ruthenium(III) salophen catalyst

M. Hatefi Ardakani¹ · M. Moghadam² · S. Saeednia¹ · Z. Pakdin-Parizi¹

Received: 28 April 2015 / Accepted: 2 November 2015 / Published online: 17 November 2015
© The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract In the present study, preparation, characterization, and catalytic activity of $\text{Ru}(\text{salophen})\text{Cl}$ supported on chitosan were investigated. The prepared heterogeneous catalyst was characterized by diffuse reflectance UV–vis and FT-IR spectroscopic techniques, scanning electron microscopy, and neutron activation analysis. In this catalytic system, the effects of different solvents were studied in the epoxidation of *cis*-cyclooctene and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ was found to be a better solvent. Also, the effects of oxygen donors such as NaIO_4 , H_2O_2 , $\text{H}_2\text{O}_2/\text{urea}(\text{UHP})$, *tert*- BuOOH , NaClO , and Bu_4NIO_4 were studied in the epoxidation of *cis*-cyclooctene and NaIO_4 was selected as an oxidant. The catalytic activity of this new heterogeneous catalyst in the epoxidation of cyclic and linear alkenes using NaIO_4 as an oxidant in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at room temperature was studied. The obtained results led us to conclude that $[\text{Ru}(\text{salophen})\text{Cl}@ \text{chitosan}]$ is an efficient catalyst for the epoxidation of alkenes with NaIO_4 . The catalyst can be readily recovered simply by filtration and reused several times without any significant loss in its catalytic activity.

Keywords $\text{Ru}(\text{III})\text{salophen}$ · Chitosan · Alkene epoxidation · Sodium periodate · Heterogeneous catalyst

Introduction

Transition metal Schiff base complexes have been widely used as homogeneous or heterogeneous catalysts in various reactions such as aliphatic and aromatic hydroxylation, olefin epoxidation, and alcohol oxidation [1–27]. Although homogeneous catalysts exhibit high catalytic activity in many organic reactions, recovery and recycling of these catalysts are difficult because of oxidation of ligand or formation of dimericperoxo-species and μ -oxospecies [28]. Immobilization of homogeneous catalysts on a solid support enables easy recovery and recycling of homogeneous catalysts and avoids their disadvantages with respect to handling and reusability of the catalyst [29]. Recently, ruthenium complexes have been developed as suitable catalysts in organic synthesis [30–35]. Also, Schiff base complexes of ruthenium(III) are used as potential catalysts for olefin epoxidation [36].

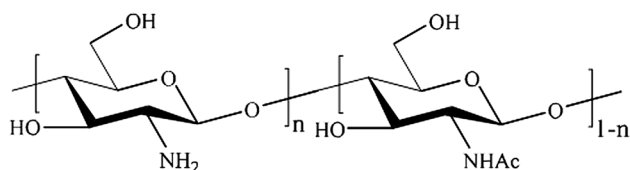
Chitosan is a linear copolymer in which 2-amino-2-deoxy-D-glucopyranose (glucosamine) is linked to 2-acetamido-2-deoxy-D-glucopyranose (*N*-acetylglucosamine) by a β -(1,4) glycosidic bond (Scheme 1). Chitosan is produced by *N*-deacetylation of chitin, which is easily obtained from crab or shrimp. This natural polymer has many good properties such as biocompatibility, biodegradability, and non-toxicity, which make it an environmental-friendly material. Furthermore, it has high percentage of nitrogen and optical chiral sites in its molecular framework [37]. Recently, the novel applications of chitosan as natural support have been reported [37–42].

The present paper describes the preparation, characterization, and catalytic activity of ruthenium(III) salophen supported on chitosan in the epoxidation of alkenes using sodium periodate at room temperature. As far as we know, our study is the first to use chitosan as support for $\text{Ru}(\text{salophen})\text{Cl}$ complex in heterogeneous catalysis.

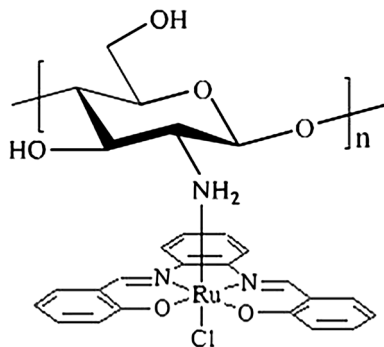
✉ M. Hatefi Ardakani
m.hatefi@vru.ac.ir

¹ Department of Chemistry, Faculty of Science, Vali-e-Asr University of Rafsanjan, 77188-97111 Rafsanjan, Iran

² Catalysis Division, Department of Chemistry, University of Isfahan, 81746-73441 Isfahan, Iran



Scheme 1 Chemical structure of the chitosan, n : degree of the acetylation



Scheme 2 Proposed structure of [Ru(salophen)Cl@chitosan]

Experimental

Chitosan was obtained from Sigma-Aldrich (viscometric average molecular weight is about 250,000, degree of deacetylation $\geq 75\%$). Other materials were purchased from Fluka and Merck chemical companies. FT-IR spectra obtained as KBr pellets were in the range of 400–4000 cm^{-1} when observed using Nicolet-iS10 spectrometer. Diffuse reflectance spectrum was recorded on a Shimadzu UV-265 instrument using optical-grade BaSO_4 as reference. Scanning electron micrographs of the catalyst and support were taken on a SEM Philips XL30 instrument. Gas chromatography experiments (GC) were performed with Philips GC-PU 4600 instrument using a 2-m column packed with silicon DC-200 and FID detector. *n*-Decane was used as internal standard. The salophen ligand was prepared by refluxing the ethanolic solutions of 1,2-phenylenediamine and salicylaldehyde in a 1:2 molar ratio and metallated with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ [43, 44].

Preparation of the catalyst, [Ru(salophen)Cl@chitosan]

A mixture of chitosan (2 g) in acetic acid (2 %, 100 ml) was stirred electromagnetically at 323 K for 0.5 h. Then distilled water (100 ml) was added to form a colloidal solution. The pH of the solution was adjusted to 8 by the addition of an aqueous solution of Na_2CO_3 (1 %). Then, Ru(salophen)Cl (0.45 g, 1 mmol) was dissolved in CH_3CN (50 ml) and was added drop-wise to the first solution. After stirring for 24 h in these conditions, the light-brown solids

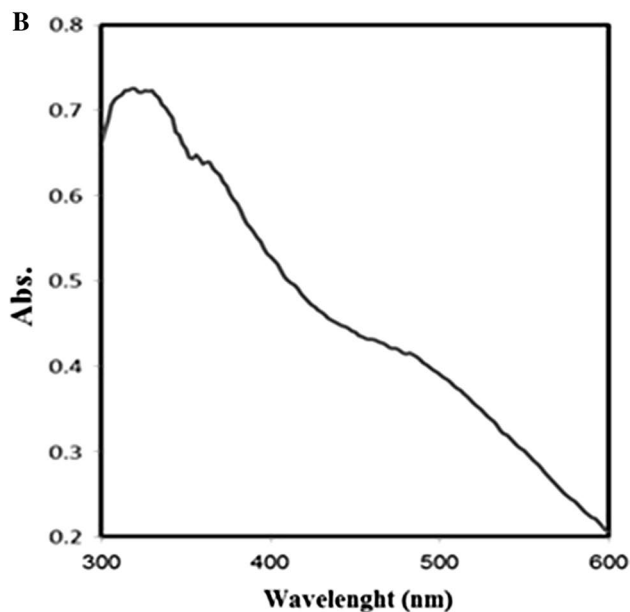
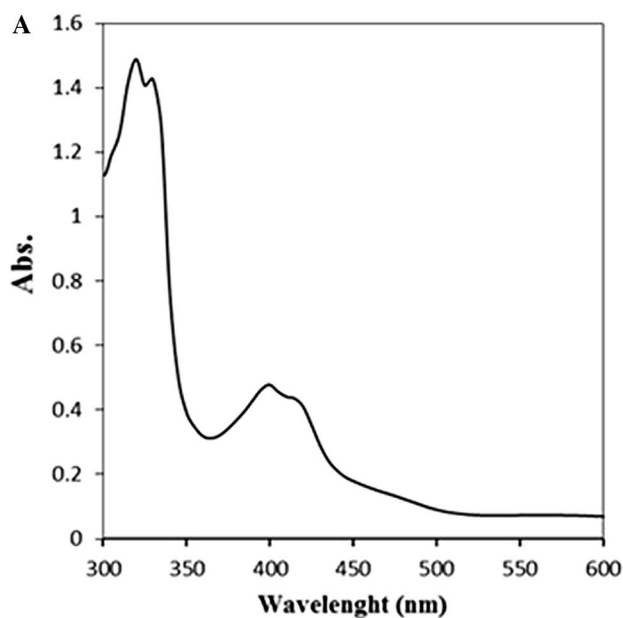


Fig. 1 UV-Vis spectrum of **a** Ru(salophen)Cl and **b** [Ru(salophen)Cl@chitosan]

were separated by filtration, washed with distilled water, ethanol, and acetone successively, and dried at 80 °C for 8 h to yield the chitosan-supported ruthenium(III) salophen.

General procedure for catalytic epoxidation of alkenes with NaIO_4 catalyzed by [Ru(salophen)Cl@chitosan]

A mixture of alkene (1 mmol), catalyst (800 mg, containing 0.05 mmol Ru(salophen)Cl) in CH_3CN (5 ml), and NaIO_4 (2 mmol) in H_2O (5 ml) was prepared and stirred magnetically at room temperature. The progress of the reaction was

monitored by GC. At the end of the reaction, the reaction mixture was diluted with Et₂O (20 ml) and filtered. The catalyst was thoroughly washed with Et₂O, and the combined washings and filtrates were purified on silica gel plates or a silica-gel column. IR and ¹H NMR spectral data confirmed the identities of the products.

Results and discussion

Preparation and characterization of catalyst, [Ru(salophen)Cl@chitosan]

The supported catalyst, [Ru(salophen)Cl@chitosan], seemed to have been formed by interaction between the amino groups of chitosan and ruthenium atoms of

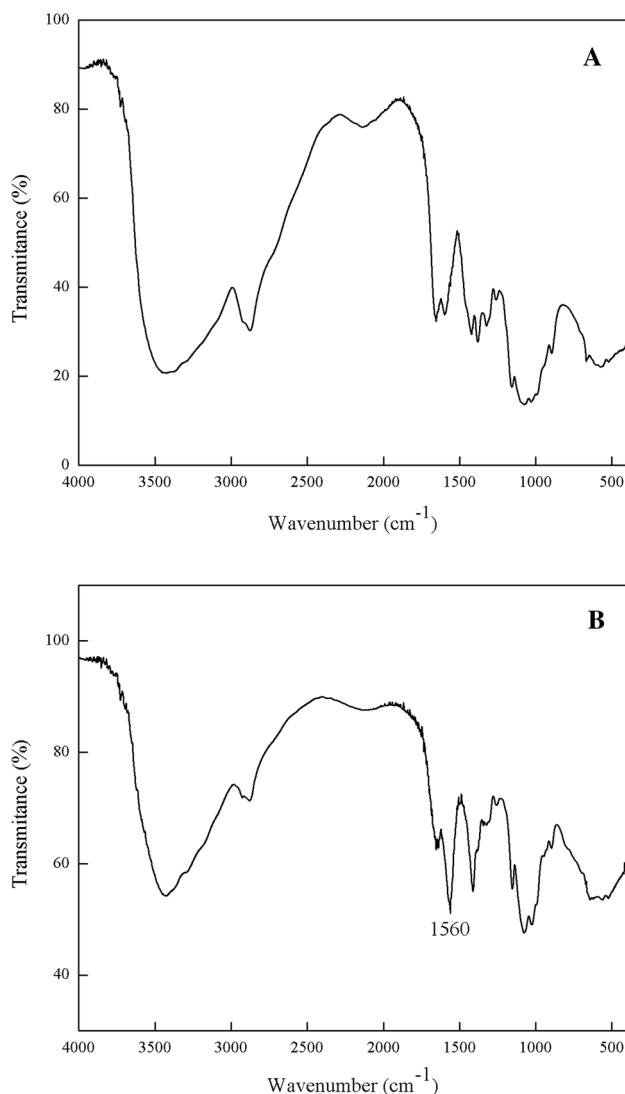


Fig. 2 FT-IR spectrum of **a** chitosan and **b** [Ru(salophen)Cl@chitosan]

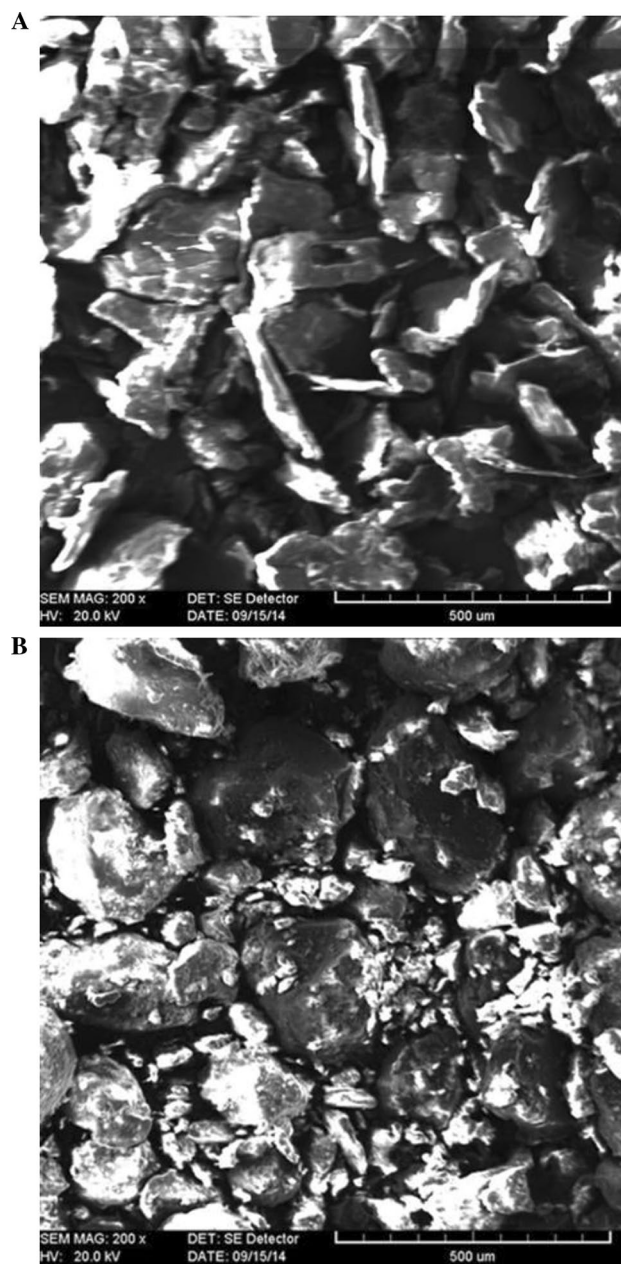


Fig. 3 Scanning electron micrograph of **a** chitosan and **b** [Ru(salophen)Cl@chitosan]

Ru(salophen)Cl (Scheme 2) [45]. The presence of a large number of amine groups on the chitosan explains the uptake of metal cations on the free electronic doublet of nitrogen at near neutral pH [46]. The new heterogeneous catalyst [Ru(salophen)Cl@chitosan] was characterized by FT-IR spectroscopy, diffuse reflectance UV–Vis spectroscopy, scanning electron microscopy (SEM), and neutron activation analysis (NAA). The Ru content of catalyst, determined by NAA, was found to be about 0.065 mmol g⁻¹.

The UV–Vis spectra of Ru(salophen)Cl and [Ru(salophen)Cl@chitosan] were recorded in the range of 300–600 nm. In

this region, Ru(salophen)Cl showed a sharp peak and a shoulder at 325 and 397 nm which can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [25] (Fig. 1a). These peaks were observed with only a slight shift at 318 and 370 nm in the UV–Vis spectra of [Ru(salophen)Cl@chitosan] (Fig. 1b). This confirmed the presence of metallocomplex on the support.

The FT-IR spectrum provided further evidence for attachment of Ru(salophen)Cl to the support. The FT-IR spectrum of [Ru(salophen)Cl@chitosan] shows a band at 1560 cm^{-1} which is not observed in the FT-IR spectrum of pure chitosan. This band belongs to azomethine ($\text{C}=\text{N}$) stretching vibration in the salophen ligand (Fig. 2).

The SEM images of the chitosan and [Ru(salophen)Cl@chitosan] showed a clear change in morphology of the chitosan after introducing to salophen complex (Fig. 3).

Catalytic activity

First, in order to achieve the suitable reaction conditions, the reaction parameters were optimized in the epoxidation of cyclooctene.

Effects of oxidants on the epoxidation of cyclooctene catalyzed by [Ru(salophen)Cl@chitosan]

Different oxygen donors such as NaIO_4 , H_2O_2 , $\text{H}_2\text{O}_2/\text{urea}$ (UHP), *tert*-BuOOH, NaClO, and Bu_4NIO_4 were used for the epoxidation of cyclooctene in the presence of [Ru(salophen)Cl@chitosan]. The results showed that NaIO_4 is the best oxidant because of its good oxidation conversion and inertness in the absence of catalyst (Table 1).

Effects of solvents on the epoxidation of cyclooctene catalyzed by [Ru(salophen)Cl@chitosan]

Among the mixture of acetonitrile, methanol, ethanol and acetone (single-phase systems), and dichloromethane (two-phase system with *n*-Bu₄NBr as phase-transfer catalyst)

Table 1 Effects of oxidants on the epoxidation of cyclooctene catalyzed by [Ru(salophen)Cl@chitosan] at room temperature

Row	Oxidant	Solvent	Epoxide yield (%)	Time (h)
1	NaIO_4	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	73	24
2	H_2O_2	CH_3CN	25	24
3	$\text{H}_2\text{O}_2/\text{urea}$	CH_3CN	38	24
4	<i>tert</i> -BuOOH	CH_3CN	17	24
5	NaOCl	CH_3CN	41	24
6	Bu_4NIO_4	CH_3CN	10	24
7	No oxidant	CH_3CN	trace	24

Reaction conditions: cyclooctene (1 mmol), oxidant (2 mmol), catalyst (800 mg, containing 0.05 mmol Ru(salophen)Cl), CH_3CN (5 ml), H_2O (5 ml)

with water, a 1:1 mixture of acetonitrile/water was found to have the highest catalytic activity. The results are shown in Table 2.

Catalytic alkene epoxidation with NaIO_4 in the presence of [Ru(salophen)Cl@chitosan]

The catalytic activity of this catalyst was investigated in the epoxidation of different alkenes such as linear, cyclic, and phenyl-substituted ones. The epoxidation reaction was performed at room temperature with NaIO_4 in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (Scheme 3). In the epoxidation of cyclooctene with NaIO_4 in the presence of [Ru(salophen)Cl@chitosan] after 24 h, the conversion was 73 % with 100 % selectivity. Cyclohexene was oxidized with yields of 68 and 85 % epoxide selectivity. The cyclohexene-1-one as a by-product was detected in the reaction mixture. In the epoxidation of styrene and α -methylstyrene, the conversion was 65 and 58 %, and the epoxide selectivities were 78 and 81 %, respectively. In the oxidation of styrene and α -methylstyrene, benzaldehyde and acetophenone were produced as by-products, respectively.

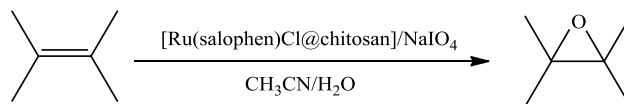
In the case of indene, the selectivity was 100 %. Linear alkenes such as 1-heptene and 1-dodecene were converted to their corresponding epoxides with 100 % selectivity (Table 3). Blank experiments in the absence of catalyst were also investigated. The obtained results showed that the alkenes were not epoxidized in the absence of catalyst or oxidant.

Table 2 Effects of solvents on the epoxidation of cyclooctene with NaIO_4 catalyzed by [Ru(salophen)Cl@chitosan] at room temperature

Row	Solvent	Epoxide yield (%)	Time (h)
1	$\text{CH}_3\text{CN}/\text{H}_2\text{O}(1:1)$	73	24
2	$\text{CH}_3\text{CN}/\text{H}_2\text{O}(2:1)^a$	61	24
3	$\text{CH}_3\text{OH}/\text{H}_2\text{O}$	27	24
4	$\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$	20	24
5	$\text{CH}_3\text{COCH}_3/\text{H}_2\text{O}$	14	24
6	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$	11	24






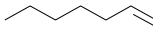
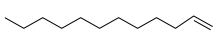
Reaction conditions: cyclooctene (1 mmol), NaIO_4 (2 mmol), catalyst (800 mg, containing 0.05 mmol Ru(salophen)Cl), solvent (5 ml), H_2O (5 ml)

^a CH_3CN (5 ml) and H_2O (2.5 ml)



Scheme 3 Alkene epoxidation with NaIO_4 catalyzed by [Ru(salophen)Cl@chitosan]

Table 3 Epoxidation of alkenes with NaIO₄ catalyzed by [Ru(salophen)Cl@chitosan]

Entry	Alkene	Conversion (%) ^a	Epoxide selectivity(%) ^a	Time (h)
1		73	100	24
2		68 ^b	85	24
3		65 ^c	78	24
4		58 ^d	81	24
5		45	100	24
6		35	100	24
7		32	100	24

^a GLC yield based on the starting alkene^b The by-product is allylic ketone^c The by-product is benzaldehyde^d The by-product is acetophenone**Table 4** The results of catalyst recovery and the amounts of ruthenium leached in the epoxidation of cyclooctene with NaIO₄

Run	Epoxide yield (%) ^a	Time (h)	Ru leached (%) ^b
1	73	24	4
2	72	24	2.7
3	71	24	1
4	71	24	0
5	69	24	0

^a GLC yield based on starting alkene^b Determined by atomic absorption spectroscopy

Catalyst reusability

Since the transition metal complexes are often expensive to purchase or prepare, we decided to investigate the reusability of catalyst in the epoxidation reactions. In this manner, the reusability of [Ru(salophen)Cl@chitosan] was studied in the epoxidation of cyclooctene. After each experiment, the catalyst was separated from the reaction mixture simply by filtration, washed thoroughly with CH₃CN and Et₂O, and dried before using it in the subsequent run. The filtrates were used for the determination of ruthenium leaching by atomic absorption spectroscopy (AAS). The results showed that in the first three runs, some Ru is leached from the support (Table 4).

Conclusions

Ru(salophen)Cl supported on chitosan is an efficient catalyst for the epoxidation of alkenes with NaIO₄ under

agitation with magnetic stirring. This new heterogeneous catalyst has the advantages such as easy preparation, facile and effective recovery, and recycling of the catalyst. Also, chitosan is a natural and cheap support and possesses particular microstructure and excellent function.

Acknowledgments The support of this work by Vali-e-Asr University of Rafsanjan is acknowledged.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- W. Zhang, E.N. Jacobsen, *J. Org. Chem.* **56**, 2296 (1991)
- G.T. Musie, M. Wei, B. Subramanian, D.H. Busch, *Inorg. Chem.* **40**, 3336 (2001)
- D. Dolphin, T.G. Traylor, L.Y. Xie, *Acc. Chem. Res.* **30**, 251 (1997)
- T. Uchida, T. Katsuki, *Tetrahedron Lett.* **42**, 6911 (2001)
- A. Zsigmond, A. Horvath, F. Notheisz, *J. Mol. Catal. A: Chem.* **171**, 95 (2001)
- H. Aneetha, J. Padmaja, P.S. Zacharias, *Polyhedron* **15**, 2445 (1996)
- R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, P.K. Iyer, R.V. Jasra, *J. Catal.* **209**, 99 (2002)
- C.M. Che, J.S. Huang, *Coord. Chem. Rev.* **242**, 97 (2003)
- H. Imanishi, T. Katsuki, *Tetrahedron Lett.* **38**, 251 (1997)
- T. Katsuki, *J. Mol. Catal. A: Chem.* **113**, 87 (1996)
- L. Canalai, D.C. Sherrington, *Chem. Soc. Rev.* **72**, 603 (1999)
- E.C. Song, S. Li, *Chem. Rev.* **102**, 3495 (2002)

13. T. Piacham, C. Isarankura, V. Rachayasittikul, L. Bulow, L. Ye, *Chem. Commun.* (11), 1254 (2003)
14. M.R. Maurya, S.J. Titinchi, S. Chand, *J. Mol. Catal. A: Chem.* **180**, 201 (2002)
15. K. Masutani, T. Uchida, R. Irie, T. Katsuki, *Tetrahedron Lett.* **41**, 5119 (2000)
16. K.C. Gupta, A.K. Sutar, *J. Mol. Catal. A: Chem.* **280**, 173 (2008)
17. J.A. Labinger, *J. Mol. Catal. A: Chem.* **220**, 27 (2004)
18. M.K. Dalal, R.N. Ram, *J. Mol. Catal. A: Chem.* **159**, 285 (2000)
19. S. Kulkarni, M. Alurkar, A. Kumar, *Appl. Catal. A: Gen.* **142**, 243 (1996)
20. V. Mirkhani, S. Tangestaninejad, M. Moghadam, M. Moghbel, *Bioorg. Med. Chem.* **12**, 4673 (2004)
21. V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, *Appl. Catal. A: Gen.* **311**, 43 (2006)
22. G. Grivani, S. Tangestaninejad, A. Halili, *Inorg. Chem. Commun.* **10**, 914 (2007)
23. M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, M. MoshrefJavadi, *Polyhedron* **29**, 648 (2010)
24. S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, M.S. Saeedi, *Appl. Catal. A: Gen.* **381**, 233 (2010)
25. M. Moosavifar, S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, *J. Mol. Catal. A: Chem.* **377**, 92 (2013)
26. M. Torki, S. Tangestaninejad, V. Mirkhani, M. Moghadam, I. Mohammadpoor-Baltork, A. R. Khosropour, *J. Inorg. Organomet. Polym.* **23**, 923 (2013)
27. S. Rayati, P. Abdollahian, *Compt. Rend. Chim.* **16**, 814 (2013)
28. J.P. Collman, V.J. Lee, C.J. Kellen-Yuen, X. Zhang, J.A. Brauman, *J. Am. Chem. Soc.* **117**, 692 (1995)
29. D.E. Devos, M. Dams, B. F. Sels, P.A. Jacobs, *Chem. Rev.* **102**, 3615 (2002)
30. R. Sanz, D. Miguel, A. Martinez, J.M. Alvarez-Gutierrez, F. Rodriguez, *Org. Lett.* **9**, 202 (2007)
31. B.M. Trost, R.C. Livingston, *J. Am. Chem. Soc.* **130**, 11970 (2008)
32. H. Fuwa, K. Noto, M. Sasaki, *Org. Lett.* **12**, 1636 (2010)
33. F. Kakiuchi, T. Kochi, E. Mizushima, S. Murai, *J. Am. Chem. Soc.* **132**, 17741 (2010)
34. N.P. Hiatt, J.M. Lynam, C.E. Welby, A.C. Whitwood, *J. Org. Chem.* **696**, 378 (2011)
35. B. Barati, M. Moghadam, A. Rahmati, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, *Catal. Commun.* **29**, 122 (2012)
36. R. Antony, G.L. Tembe, M. Ravindranathan, R.N. Ram, *Polymer* **39**, 4327 (1998)
37. H. Wang, W. Sun, C. Xia, *J. Mol. Catal. A: Chem.* **206**, 199 (2003)
38. C.-C. Guo, G. Huang, X.-B. Zhang, D.-C. Cuo, *Appl. Catal. A: Gen.* **247**, 261 (2003)
39. G. Huang, Y.-A. Guo, H. Zhou, S.-K. Zhao, S.-Y. Liu, A.-P. Wang, J.-F. Wei, *J. Mol. Catal. A: Chem.* **273**, 144 (2007)
40. S.E.S. Leonhardt, A. Stole, B. Ondruschka, G. Crarotto, C. Deleo, K.D. Jandt, T.F. Keller, *Appl. Catal. A: Gen.* **379**, 30 (2010)
41. S. Schubler, N. Blaubach, A. Stole, G. Cravotto, B. Ondruschka, *Appl. Catal. A: Gen.* **445–446**, 231 (2012)
42. J. Tong, Y. Zhang, Z. Li, C. Xia, *J. Mol. Catal. A: Chem.* **249**, 47 (2006)
43. D. Chan, A.E. Martell, *Inorg. Chem.* **26**, 1026 (1987)
44. B.M. Trivedi, P.K. Bhattacharya, P.A. Ganeshpure, S. Satish, *J. Mol. Catal.* **75**, 109 (1992)
45. D.J. Macquarrie, J.E. Hardy, *Ind. Eng. Chem. Res.* **44**, 8499 (2005)
46. E. Guibal, *Prog. Polym. Sci.* **30**, 71 (2005)