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Silica supported Ru(salophen)Cl: An efficient and robust heterogeneous catalyst for epoxidation of alkenes with sodium periodate

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ABSTRACT

In the present work, heterogenization of Ru(salophen)Cl via its axial ligation to silica-bound imidazole, SiIm, is reported. The heterogeneous catalyst, [Ru(salophen)Cl–SiIm], was characterized by elemental analysis, SEM, TEM, FT-IR and diffuse reflectance UV–Vis spectroscopic techniques. The catalyst, which is not soluble in water and common organic solvents, was used for efficient epoxidation of cyclic and linear alkenes with $NaIO_4$ under agitation with magnetic stirring. This new heterogenized catalyst is of high stability and reusability in the oxidation reactions. The effect of reaction parameters such as solvent and oxidant in the epoxidation of *cis*-cyclooctene were also investigated.

1. Introduction

Ruthenium complexes have been known as versatile electron-transfer and energy-transfer compounds [1–22]. Due to these unique characteristics, ruthenium complexes exhibit a wide range of applications in various research areas such as artificial photosynthesis, photomolecular devices, probes for biological macromolecules, oxidation catalysts and organic synthesis [8–22].

In the last two decades, salen and salophen ligands bearing *O* and *N* donor atoms and their complexes have received much attention, mainly because of their extensive applications in the fields of synthesis and catalysis [23–26]. Homogeneous catalysts are not recoverable and degrade in the reaction media and therefore contaminate the products. But their heterogeneous counterparts present many advantages such as easy separation and recovery of the catalyst, and higher stability of the catalytic species. Different approaches such as non-covalent immobilization in zeolites, clay or siloxane membranes [27–32], covalent grafting onto inorganic supports such as silica or MCM-41 [33–37], co-polymerization of a functionalized salen monomer into an organic polymer [38], attachment or build-up of a salen structure to a performed polymer [39–44], and axial ligation to surface bound ligands [45–47] have been reported for immobilization of Schiff base complexes (salen or salophen) on the supports.

Co(salen) has been used by Jacobsen group as a highly efficient catalyst for hydrolytic kinetic resolution of racemic epoxides and enantioselective parallel synthesis [48,49].

In comparison with modified resins, modified silica exhibits some advantages such as higher surface area, higher thermal and chemical stability.

In continuation of our research on the preparation of supported Schiff base catalysts [46,47,50–54], here, we report the preparation, characterization and investigation of catalytic activity of [Ru(salophen)Cl] supported on silica-bound imidazole in the epoxidation of alkene with sodium periodate at room temperature (Scheme 1).

2. Experimental

All materials were commercial reagent grade. 3-Chloropropyl-functionlized silica gel (230–400 mesh, 2.5% Cl, 0.714 mmol/g) was purchased from Aldrich. Alkenes obtained from Merck or Fluka

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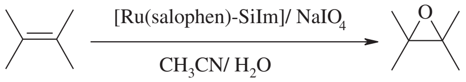


Scheme 1.

and were passed through a short column containing active alumina to remove the peroxidic impurities. Diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade $BaSO_4$ as the reference. FT-IR spectra obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with a Nicolet-Impact 400D spectrometer. Scanning electron micrographs of the catalyst and silica were taken on a SEM Philips XL 30 instrument. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20m and *n*-decane was used as internal standard. ^{1}H NMR spectra were recorded with a Bruker-Arance AQS 300 MHz.

The Schiff base ligand was prepared by the standard procedure of refluxing ethanolic solutions of the 1,2-phenylenediamine and salicylaldehyde in a 1:2 molar ratio and metallated with $RuCl_3 \cdot 3H_2O$ [55,56]. Silica surface modification with imidazole to give the SiIm was carried out through the method described by Lindsay and co-workers [57].

2.1. Preparation of silica-supported ruthenium salophen, [Ru(salophen)Cl–SiIm]

To a solution of ruthenium(III) salophen (0.45 g, 1 mmol) in CH_3CN (50 ml) was added silica-bound imidazole (3 g). The mix-

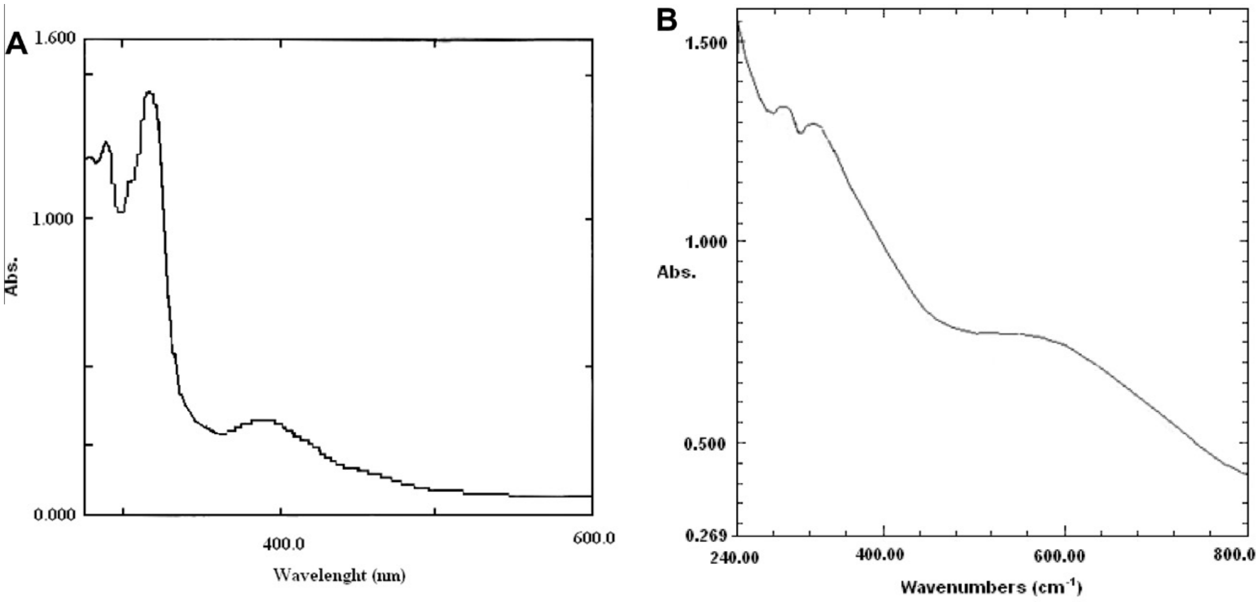
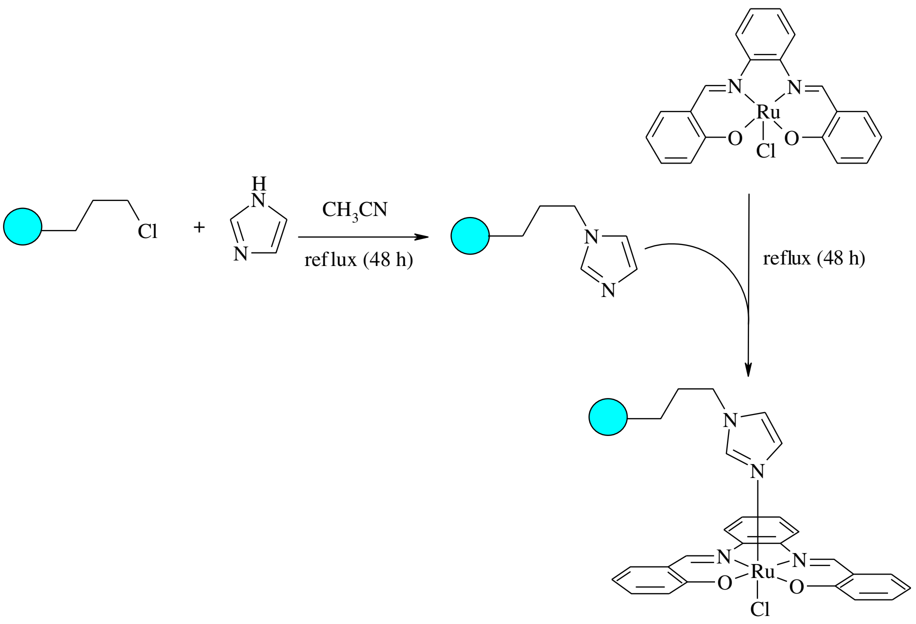


Fig. 1. UV–Vis spectrum of: (A) non-supported catalyst and (B) [Ru(salophen)Cl–SiIm].



Scheme 2. Preparation of silica supported [Ru(salophen)Cl].

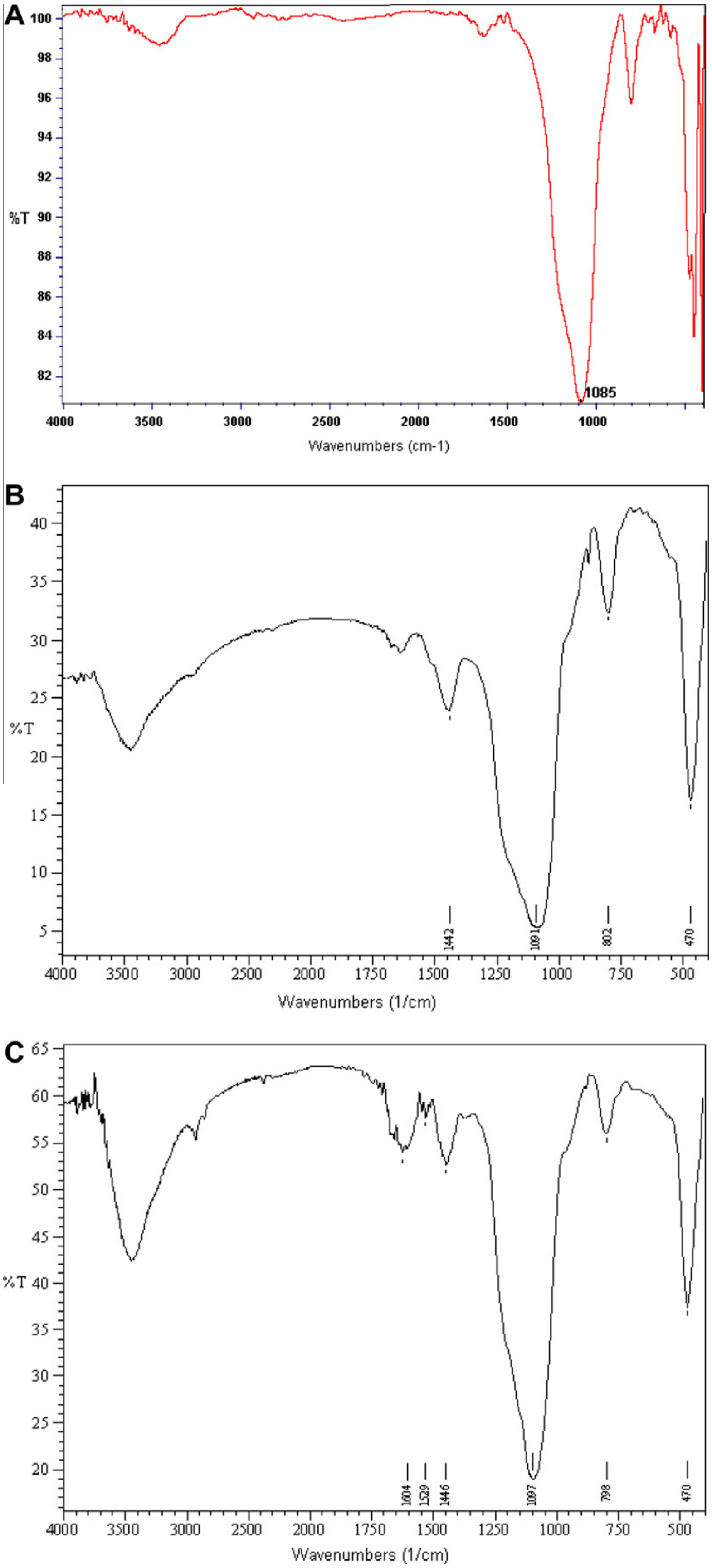


Fig. 2. FT-IR spectrum of: (A) chloropropylated silica; (B) SiIm and (C) [Ru(salophen)Cl–SiIm].

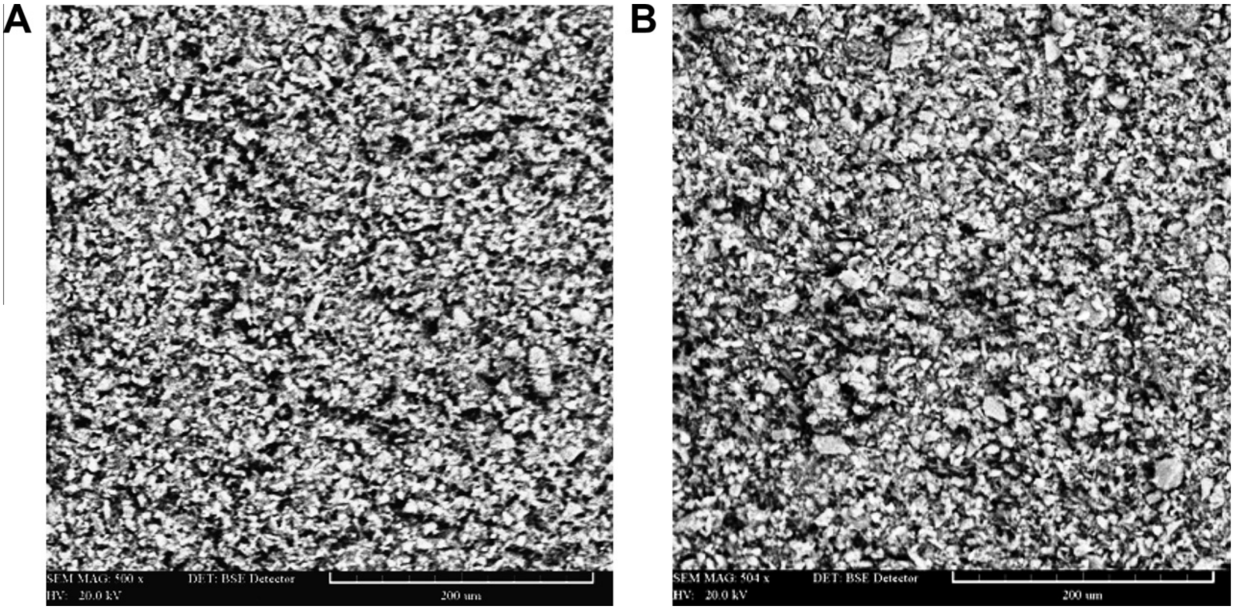


Fig. 3. Scanning electron micrograph of: (A) SiIm and (B) [Ru(salophen)–SiIm].

ture was vigorously stirred at 80 °C for 24 h. After cooling, the brown silica particles were collected by filtration, washed thoroughly with acetonitrile, methanol, and ether successively, and dried at room temperature for several hours.

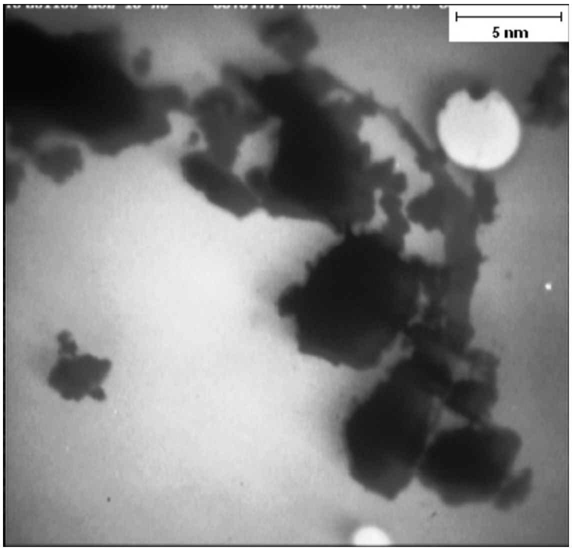


Fig. 4. Transmission electron micrograph of [Ru(salophen)–SiIm].

Table 1
Effect of oxidant on the epoxidation of cyclooctene catalyzed by [Ru(salophen)Cl–SiIm] at room temperature. [a]

Row	Oxidant	Solvent	Epoxide yield (%)	Time (h)
1	$NaIO_4$	CH_3CN/H_2O	95	4
2	H_2O_2	CH_3CN	43	4
3	H_2O_2/urea	CH_3CN	19	4
4	NaOCl	CH_3CN	33	4
5	*tert*-BuOOH	CH_3CN	64	4
6	Bu_4NIO_4	CH_3CN	40	4

[a] Cyclooctene (0.5 mmol), oxidant (1 mmol), catalyst (300 mg, 0.034 mmol), CH_3CN (5 ml), H_2O (5 ml).

Table 2
Effect of solvent on epoxidation of cyclooctene with $NaIO_4$ catalyzed by [Ru(salophen)Cl–SiIm] at room temperature.[a]

Row	Solvent	Epoxide yield (%)	Time (h)
1	CH_3CN/H_2O (1:1)	95	3
2	CH_3CN/H_2O (2:1)[b]	70	3
3	CH_3COCH_3/H_2O	47	3
4	CH_3OH/H_2O	75	3
5	CH_3CH_2OH/H_2O	55	3
6	CH_2Cl_2/H_2O	26	3
7	CCl_4/H_2O	12	3

[a] Cyclooctene (0.5 mmol), $NaIO_4$ (1 mmol), catalyst (0.025 mmol), solvent (5 ml), H_2O (5 ml).
[b] CH_3CN (5 ml) and H_2O (2.5 ml).

2.2. General procedure for catalytic epoxidation of alkenes with sodium periodate catalyzed by [Ru(salophen)Cl–SiIm]

In a 25 ml flask equipped with a magnetic stirrer bar, a mixture of alkene (0.5 mmol), [Ru(salophen)Cl–SiIm] (250 mg, 0.026 mmol) in CH_3CN (5 ml) and $NaIO_4$ (1 mmol) in H_2O (5 ml) was prepared and stirred at room temperature. The progress of the reaction was monitored by GC. At the end of the reaction, the reaction mixture was diluted with Et_2O (20 ml). The catalyst was filtered, washed thoroughly with Et_2O and combined washings and filtrates were purified on a silica-gel plates or a silica-gel column. IR and ^1H NMR spectral data confirmed the identities of the products. Blank experiments with the same experimental conditions in the absence of catalyst were also performed.

3. Results and discussion

3.1. Preparation and characterization of silica-bound ruthenium(III) salophen catalyst, [Ru(salophen)Cl–SiIm]

The supported ruthenium catalyst, [Ru(salophen)–SiIm], was obtained by stirring a suspension of SiIm in a solution of the [Ru(salophen)Cl] in dichloromethane (Scheme 2). The silica-bound imidazole was characterized by elemental analysis, SEM, TEM, diffuse reflectance UV–Vis (DR UV–Vis) and FT-IR spectroscopic techniques. The nitrogen content of this support was 1.7%. According to this value, the degree of imidazole, introduced into the silica, was 0.607 mmol/g of support. This shows that 85% of total chlorines have been substituted by imidazole.

The Ru content of the supported catalyst, determined by ICP, showed a value of about 0.102 mmol per gram of supported catalyst.

The UV–Vis spectra in the diffuse reflectance mode provided further evidence for the presence of [Ru(salophen)Cl] on the silica. Absorption spectrum of homogeneous [Ru(salophen)Cl] showed peaks at 292 and 318 nm (Fig. 1A). In the diffuse reflectance spectrum of the [Ru(salophen)Cl–SiIm], these peaks were appeared at 290 and 320 nm, which clearly showed the presence of metallosalen on the surface (Fig. 1B).

Fig. 2 shows the FT-IR spectra of Silica, SiIm and [Ru(salophen)Cl–SiIm]. After introducing the imidazole to silica, the imidazole stretching band was appeared at 1442 cm^{-1} (Fig. 2A and B). Upon coordination of [Ru(salophen)Cl] to SiIm, a characteristic band at 1604 cm^{-1} (belong to $\upsilon_{C=N}$ in the salophen ligand) was observed. On the other hand, the band at 1529 cm^{-1} can be attributed to the aromatic rings in the salophen (Fig. 2C).

Scanning electron micrograph, (SEM), was recorded to understand the morphological changes on the surface of silica. The image of chloropropylated silica showed that silica particles have sizes in the micrometer range (2–10 μm). While after supporting of Ru(salophen)Cl on silica, the particle sizes reduce and smaller particles are obtained (Fig. 3). The TEM image of the prepared catalyst shows how the Ru(salophen)Cl has been distributed on the silica particles (Fig. 4). Since the image has been taken in the nanometer scale therefore the crystalline planes of silica has not been observed in the image. But it is clear that the catalytic species have a nanometer size.

3.2. Catalytic activity

First, in order to attain the highest catalytic activity, the reaction parameters were optimized in the epoxidation of cyclooctene.

3.2.1. Effect of terminal oxidants on the epoxidation of cyclooctene catalyzed by [Ru(salophen)Cl–SiIm]

Different single oxygen donors such as $NaIO_4$, H_2O_2, urea-H_2O_2 (UHP), NaOCl, *tert*-BuOOH and $(n\text{-}Bu)_4NIO_4$ were used in the epoxidation of cyclooctene in the presence of [Ru(salophen)Cl–SiIm]. The results showed that sodium periodate is the best oxygen source because of its inertness in the absence of catalyst and its high solubility in CH_3CN/H_2O mixture (Table 1).

3.2.2. Effect of solvent on the epoxidation of cyclooctene catalyzed by [Ru(salophen)Cl–SiIm]

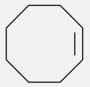
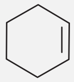
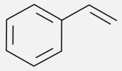
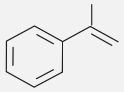
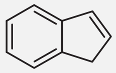
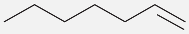
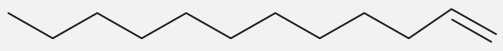
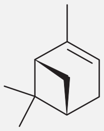
The effect of different solvents on the epoxidation of cyclooctene with $NaIO_4$ catalyzed by [Ru(salophen)Cl–SiIm] was also investigated (Table 2). Among the mixture of methanol, ethanol, acetone, and acetonitrile (single phase systems), chloroform, dichloromethane and carbon tetrachloride (two phase systems with Bu_4NBr as phase transfer catalyst) with water, the 1:1 mixture of acetonitrile/ water was chosen as the reaction medium, because the higher epoxide yield was observed. The higher catalytic activity in aqueous acetonitrile is attributed to polarity of solvent and high solubility of $NaIO_4$ in it.

3.2.3. Catalytic Alkene epoxidation with $NaIO_4$ catalyzed by [Ru(salophen)Cl–SiIm]

First, the catalytic activity of this catalyst was investigated in the epoxidation of cyclooctene with $NaIO_4$. The reaction was performed at room temperature under air in CH_3CN/H_2O. After 3 h, the yield of cyclooctene oxide was 95% with 100% selectivity. Then, under the optimized conditions, various alkenes such linear, cyclic and phenyl substituted ones were epoxidized in the presence of [Ru(salophen)Cl–SiIm] (Table 3). Cyclohexene was oxidized in 100% yield and 94% epoxide selectivity. The by-product was cyclohexene-1-one. In the case of styrene and α-methyl styrene, the conversions were 98% and 95% and the epoxide selectivities were 93% and 92%, respectively. In these systems benzaldehyde and acetopheneone were produced as by-products. This catalytic system showed a high catalytic activity in the epoxidation of linear alkenes such as 1-heptene and 1-dodecene with 100% epoxide selectivity. Finally, α-pinene was efficiently oxidized. In this system, the major product was α-pinene oxide (with 87% epoxide selectivity), and allylic oxidation products, verbenone and verbenol were produced as minor products.

Blank experiments in the presence of oxidant and using the same experimental conditions in the absence of catalyst were also investigated in the epoxidation of cyclooctene. The obtained results showed that $NaIO_4$ has poor ability to oxidize the cyclooctene. Also, no cyclooctene oxide was detected in the absence of oxidant.

Table 3
Epoxidation of alkenes with $NaIO_4$ catalyzed by [Ru(salophen)–SiIm].

Entry	Alkene	Conversion (%)[a]/	Time (h)	Epoxide selectivity (%)[a]
1		95	3	100
2		100[b]	3	94
3		98[c]	3	93
4		95[d]	3	92
5		85	4	100
6		73	8	100
7		58	8	100
8		93[e]	3	87

[a] GLC yield based on starting alkene.
[b] The by product is allylic ketone.
[c] The by product is benzaldehyde.
[d] The by product is acetophenone.
[e] The by products are 7% verbenone and 6% verbenol.

Table 4
The results of [Ru(salophen)Cl–SiIm] catalyst recovery and the ruthenium leached in the epoxidation of cyclooctene with sodium periodate.

Run	Epoxide yield (%)[a]	Time (h)[a]	Ru leached (%)[b]
1	95	3	2
2	91	3	1
3	88	3	0
4	82	3	0

[a] GLC yield based on starting alkene.
[b] Determined by ICP.

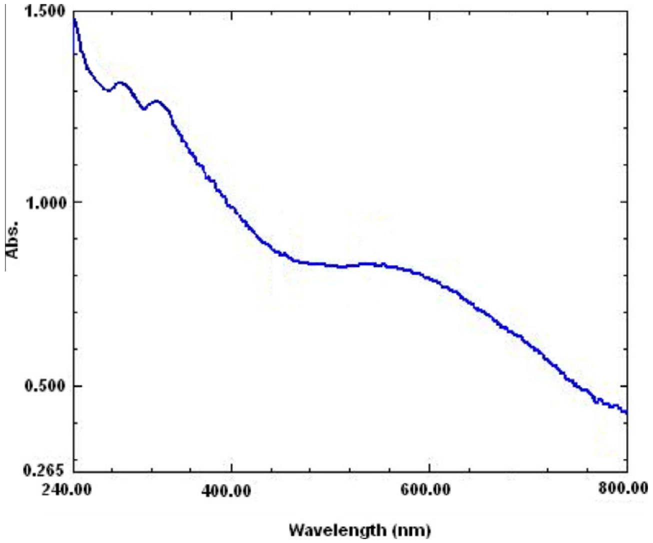


Fig. 5. The DR–UV–Vis spectrum of recovered catalyst.

3.3. Catalyst reuse and stability

Since the reusability of a catalyst is important from economical and industrial points of view, therefore, we decided to investigate the reusability and stability of [Ru(salophen)Cl–SiIm] in the oxidation reactions. In this manner, the epoxidation of cyclooctene was chosen as model reaction. After each run, the catalyst was separated from the reaction mixture by simple filtration, washed with methanol and diethyl ether and dried before using it in the subsequent run. After using the catalyst for four consecutive times, the epoxide yield was 82%.

The filtrates were used for determination of ruthenium leaching. The results showed that in the first two runs, the amount of ruthenium leached was 2% and 1%, respectively (Table 4).

The nature of the recovered catalyst was followed by DR UV–Vis spectrophotometry. The spectrum of the recovered catalyst showed no changes compared to fresh catalyst (Fig. 5).

4. Conclusion

In conclusion, Ru(salophen)Cl was successfully supported on silica-bound imidazole via axial ligation. The catalyst, [Ru(salophen)Cl–SiIm], was used as a highly efficient catalyst for alkene epoxidation with sodium periodate at room temperature. This catalyst has advantages such as easy preparation and handling of the catalyst, commercially available of the support, and facile and effective recovery and recycling of the supported catalyst.

Acknowledgements

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References

[1] E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, Elsevier, New York, 1984.
[2] G. Wilkinson, R.D. Gillard, J.A. McCleverty, Comprehensive Coordination Chemistry, vol. 4, Pergamon, Oxford, 1987. p. 277.
[3] B.K. Ghosh, A. Chakravorty, Coord. Chem. Rev. 95 (1989) 239.
[4] S.-M. Lee, W.-T. Wong, Coord. Chem. Rev. 164 (1997) 415.
[5] B.-Z. Shan, Q. Zhao, N. Goswami, D.M. Eichhorn, D.P. Rillema, Coord. Chem. Rev. 211 (2001) 117.
[6] C.E. Housecroft, Comprehensive Coordination Chemistry II, vol. 5, Elsevier Pergamon, Amsterdam, 2004.
[7] C.-M. Che, T.-C. Lau, Comprehensive Coordination Chemistry II, vol. 5, Elsevier Pergamon, Amsterdam, 2004.
[8] L. Sun, L. Hammarstrom, B. Akermark, S. Styring, Chem. Soc. Rev. 30 (2001) 36.
[9] J.N. Demas, B.A. DeGraff, Coord. Chem. Rev. 211 (2001) 317.
[10] S.E. Angell, C.W. Rogers, Y. Zhang, M.O. Wolf, W.E. Jones Jr, Coord. Chem. Rev. 250 (2006) 1829.
[11] C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408 (2000) 541.
[12] H. Tributsch, Coord. Chem. Rev. 248 (2004) 1511.
[13] N. Sardesai, S.C. Lin, K. Zimmermann, J.K. Barton, Bioconjugate Chem. 6 (1995) 302.
[14] H.B. Gray, J.R. Winkler, Annu. Rev. Biochem. 65 (1996) 537.
[15] D.B. Grotjahn, Coord. Chem. Rev. 190–192 (1999) 1125.
[16] M.J. Clarke, Coord. Chem. Rev. 236 (2003) 209.
[17] J.K. Hurst, Coord. Chem. Rev. 249 (2005) 313.
[18] C.-M. Che, Pure Appl. Chem. 67 (1995) 225.
[19] R. Zong, R.P. Thummel, J. Am. Chem. Soc. 127 (2005) 12802.
[20] T. Naota, H. Takaya, S.-I. Murahashi, Chem. Rev. 98 (1998) 2599.
[21] R. Drozdzak, B. Allaert, N. Ledoux, I. Dragutan, V. Dargutan, F. Verpoort, Coord. Chem. Rev. 249 (2005) 3055.
[22] R. Raveendran, S. Pal, Polyhedron 27 (2008) 655.
[23] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[24] T. Katsuki, J. Mol, Catal. A: Chem. 113 (1996) 87.
[25] C.T. Dalton, K.M. Ryan, V.M. Wall, C. Bousquet, D.G. Gilheany, Top. Catal. 5 (1998) 75.
[26] L. Canali, D.C. Sherrington, Chem. Soc. Rev. 28 (1999) 85.
[27] J.M. Fraile, J.I. Garcia, J. Massam, J.A. Mayoral, J. Mol. Catal. A: Chem. 136 (1998) 47.
[28] M.R. Maurya, S.J.J. Titinchi, S. Chand, I.M. Mishra, J. Mol. Catal. A: Chem. 180 (2002) 201.
[29] A. Heckel, D. Seebach, Helv. Chim. Acta 85 (2002) 913.
[30] S. Ogunwumi, T. Bein, Chem. Commun. (1997) 901.
[31] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, A. Mallekpoor-Shalamzari, Appl. Catal. A: Gen. 321 (2007) 49.
[32] B. Bahramian, V. Mirkhani, M. Moghadam, S. Tangestaninejad, Catal. Commun. 7 (2006) 289.
[33] H. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209–1210.
[34] S. Xiang, Y. Zhang, Q. Xin, C. Li, Chem. Commun. (2002) 2696–2697.
[35] B.M. Choudary, M.L. Kantam, B. Bharathi, P. Sreekanth, F. Figueras, J. Mol. Catal. A: Chem. 159 (2000) 417.
[36] C. Baleizao, B. Gigante, H. Garcia, A. Corma, J. Catal. 215 (2003) 199.
[37] G.-J. Kim, S.-H. Kim, Catal. Lett. 57 (1999) 139.
[38] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dhal, Tetrahedron: Asymmetry 6 (1995) 2105.
[39] Y.R. de Miguel, J. Chem. Soc., Perkin Trans.1 (2000) 4213–4221.
[40] G.J. Kim, D.W. Park, Catal. Today 63 (2000) 537.
[41] F. Minutolo, D. Pini, A. Petri, P. Salvadori, Tetrahedron: Asymmetry 7 (1996) 2293.
[42] L. Canali, D.C. Sherrington, H. Deleuze, React. Funct. Polym. 40 (1999) 155.
[43] S.T. Regar, K.D. Janda, J. Am. Chem. Soc. 122 (2000) 6929.
[44] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, P. Lyer, React. Funct. Polym. 34 (1997) 153.
[45] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, Appl. Catal. A: Gen. 313 (2006) 122.
[46] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, Appl. Catal. A: Gen. 311 (2006) 43.
[47] V. Mirkhani, M. Moghadam, S. Tangestaninejad, B. Bahramian, Polyhedron 25 (2006) 2904.
[48] S. Peukert, E.N. Jacobsen, Org. Lett. 1 (1999) 1245.
[49] D.A. Annis, E.N. Jacobsen, J. Am. Chem. Soc. 121 (1999) 4147.
[50] M. Moghadam, S. Tangestaninejad, M.H. Habibi, V. Mirkhani, J. Mol. Catal. A: Chem. 217 (2004) 9.
[51] M. Moghadam, S. Tangestaninejad, V. Mirkhani, H. Kargar, H. Komeili-Isfahani, Catal. Commun. 6 (2005) 688.
[52] V. Mirkhani, M. Moghadam, S. Tangestaninejad, H. Kargar, Appl. Catal. A: Gen. 303 (2006) 221.
[53] M. Hatefi, M. Moghadam, I. Sheikhshoaei, V. Mirkhani, S. Tangestaninejad, I. Mohammadpoor-Baltork, H. Kargar, Appl. Catal. A: Gen. 370 (2009) 66.
[54] S. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, M.S. Saeedi, Appl. Catal. A: Gen. 381 (2010) 233.
[55] D. Chen, A.E. Martell, Inorg. Chem. 26 (1987) 1026.
[56] B.M. Trivedi, P.K. Bhattacharya, P.A. Ganeshpure, S. Satish, J. Mol. Catal. 75 (1992) 109.
[57] R. Paul, R. Cooke, R.J. Lindsay Smith, J. Chem. Soc., Perkin Trans. 1 (1994) 1913.