RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2016, **6**, 79085

Received 22nd June 2016
Accepted 12th August 2016

DOI: 10.1039/c6ra16167g

www.rsc.org/advances

A synergistic effect of a cobalt Schiff base complex and TiO_2 nanoparticles on aerobic olefin epoxidation†

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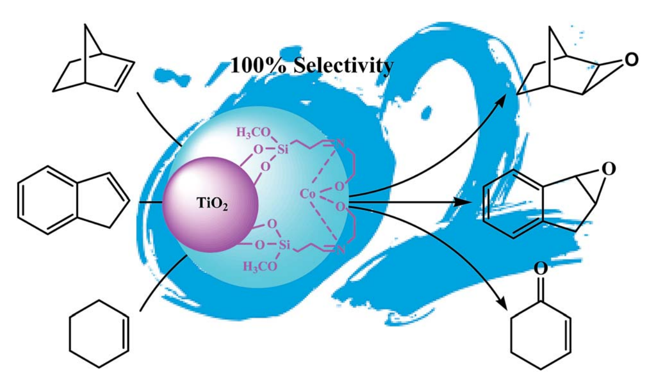
In this study, a cobalt Schiff base complex and TiO_2 nanoparticles exhibited a synergistic effect on the visible-light photocatalytic activity in the aerobic oxidation of various olefins in the absence of a reducing agent. The catalyst structure was found to be well preserved after the oxidation reaction and the catalyst could be reused at least five times.

1. Introduction

Transition metal-catalyzed aerobic oxidation reactions to produce valuable oxygen containing chemicals are an impressive example of green processes. Not only is molecular oxygen (or air) an inexpensive and renewable and the simplest available oxidant, but also the only by-product of the reaction, water, is also a non-toxic and safe chemical.[1–4]

Co-containing material catalyzed epoxidation methods have been widely developed.[5–9] The heterogeneous catalyst based-Co(II) can be easily separated, recovered, and reused from the reaction mixtures, making the processes more cost effective. Nevertheless, in many of these aerobic epoxidation reactions under the heterogeneous or homogeneous catalysis conditions, a sacrificial co-reductant was needed. Moreover, limited activity towards different olefins was observed.[7–18] Thus, there is a great demand for designing a novel heterogeneous cobalt(II)-based catalyst for aerobic epoxidation of structurally and electronically different olefins in the absence of any reducing agent.



Scheme 1 Aerobic olefin oxygenation catalyzed by $CoL_2@TiO_2$ nanohybrid.

Research on functional nanohybrid materials has been widely recognized as one of the most promising and rapidly emerging research areas in material chemistry. The unique properties of inorganic/organic nanohybrid materials can be advantageous to many fields such as optical and electronic materials, biomaterials, sensing, coating, energy storage and catalysis. To the best of our knowledge, a few reports have approached the catalytic activity of transition-metal-coordinated organic–inorganic hybrid materials for the aerobic epoxidation of olefins.[19–22]

In continuation of our ongoing research on the development of novel catalytic methods for aerobic oxidation of organic compounds,[21–24] just recently, we have discovered the catalytic efficiency of the $CoL_2@TiO_2$ nanocomposite in the selective aerobic benzylic C–H oxidation of alcohols and hydrocarbons in acetonitrile.[22] Herein, we wish to describe its catalytic activity and selectivity in the aerobic epoxidation of olefins under heterogeneous conditions, that takes place in the absence of reducing agent (Scheme 1). The catalyst was reused in the procedure for many times without any loss of activity.

2. Results and discussion

The activity of title catalyst was screened in the oxidation of norbornene (1 mmol) under continues stream of oxygen (1 atm) in acetonitrile (2 ml). No activity was observed in the absence of the catalyst under any conditions. Then, the catalytic system was performed and the influence of different factors such as solvent nature and amount, temperature, catalyst and NHPI amounts and oxidant nature on the oxidation of norbornene

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra16167g

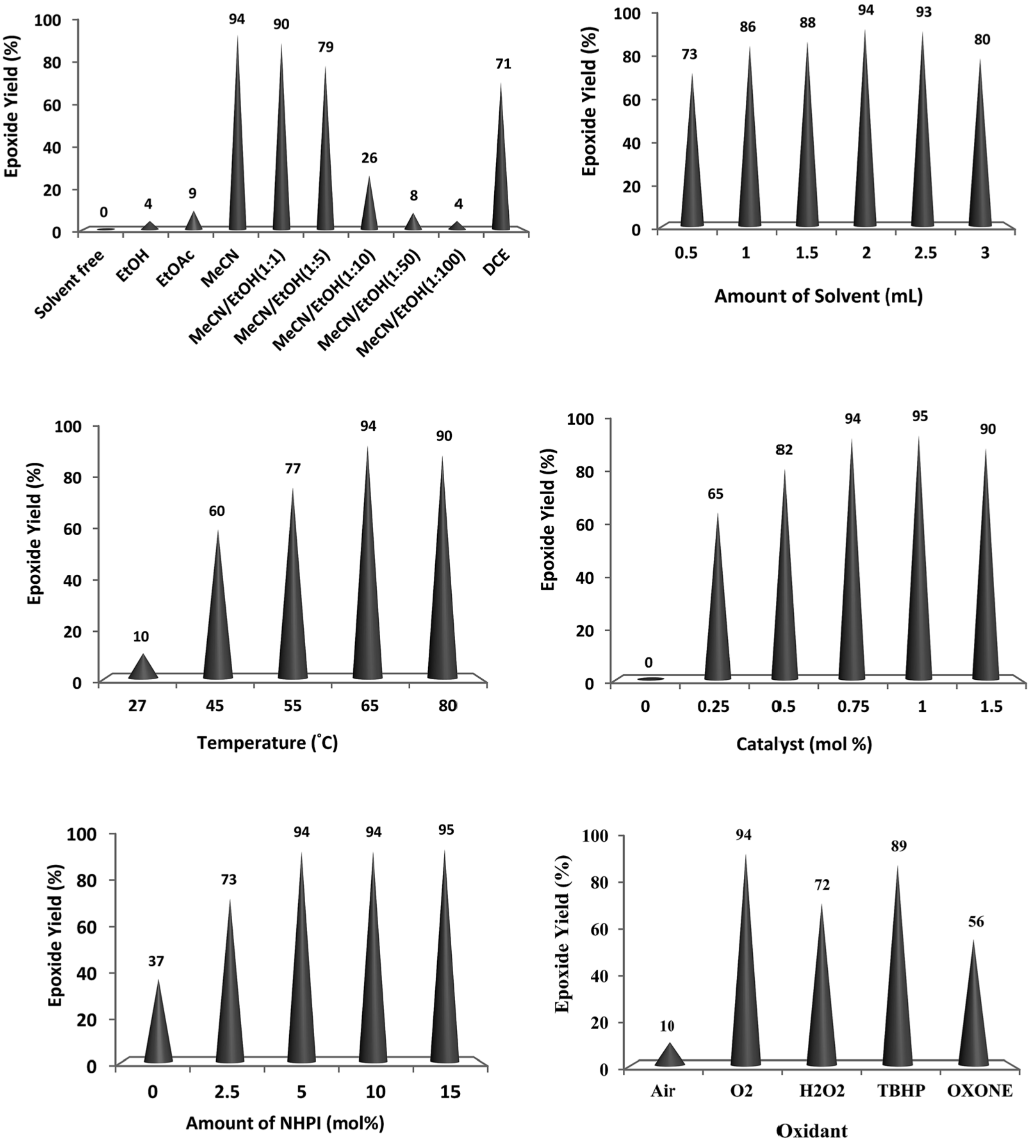


Fig. 1 The screening of the (i) solvent nature (ii) temperature (iii) solvent amount (iv) catalyst amount (v) NHPI amount and (vi) oxidant nature on the oxidation of norbornene (1 mmol) catalyzed by $CoL_2@TiO_2$ after 5 h.

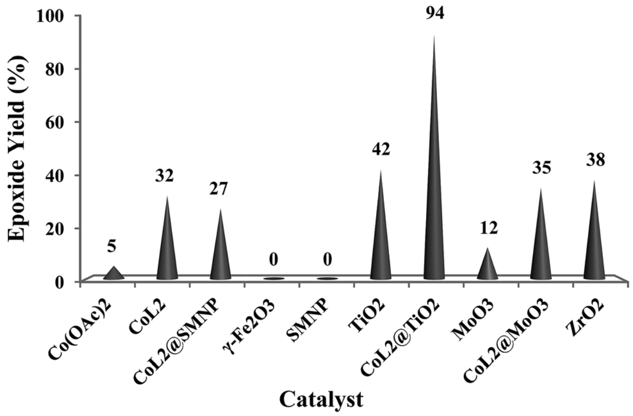


Fig. 2 The comparison of catalytic activity of $CoL_2@TiO_2$ nanocomposite with other nanocomposites and nanooxometals on the oxidation of norbornene (1 mmol) in CH_3CN (2 ml) using NHPI (5 mol%) under continues stream of O_2 (5–7 ml min^{-1}) and visible light at 65 °C.

was investigated (Fig. 1). According to our finding the catalytic system showed the best performance using a molar ratio of 100 : 5 : 0.75 for olefin–NHPI–catalyst in 2 ml acetonitrile at 65

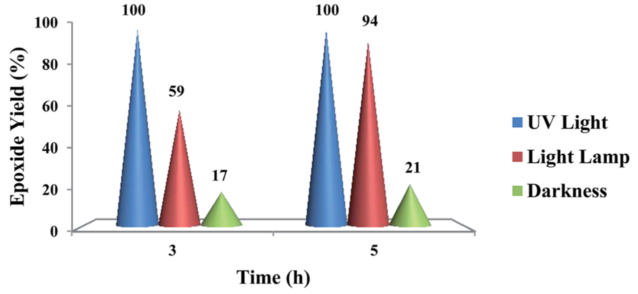


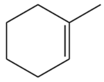
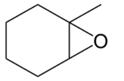
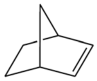
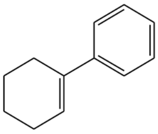
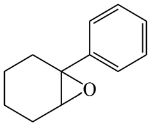
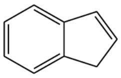
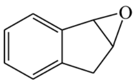
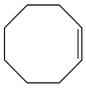
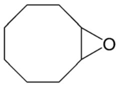
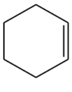
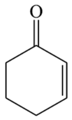
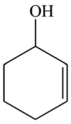
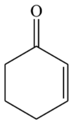
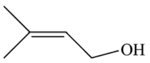
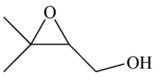
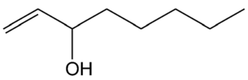
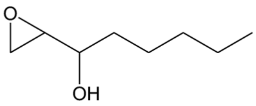
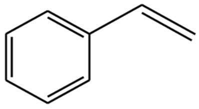
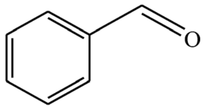
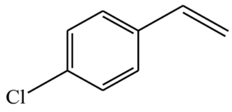
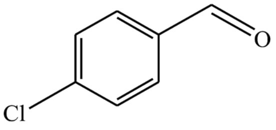
Fig. 3 The screening of photocatalytic activity of $CoL_2@TiO_2$ nanocomposite in the oxidation of norbornene using NHPI (5 mol%) under continues stream of O_2 (5–7 ml min^{-1}) at 65 °C.

°C. Under the optimized conditions, norbornene converted completely within 5 h and 96% of *exo*-norbornene oxide was secured as the sole product.

The efficiency of oxidation was affected noticeably by NHPI amount demonstrating a radical processes prevail to a high extent in the present system.[25] More evidence for this claim was obtained by retardation of the norbornene oxidation in the presence of 2,6-di-*tert*-butyl-4-methylphenol as a radical scavenger.

It is worth to mention that, replacing the catalyst (CoL_2@-TiO_2 nanocomposite) by Co-complex (CoL_2) and TiO_2 nanoparticles alone decreased the yield of norbornene oxide to 32 and 42% respectively in the presence of NHPI under the same conditions (Fig. 2). Also, another nanosized oxometals such as

Table 1 Aerobic oxidation of olefins catalyzed by CoL_2@TiO_2 nanohybrid in CH_3CN[a]

Entry	Alkene	Conversion (yield%)	Product[b]	Selectivity (%)	Time (h)
1		100 (95)		100	5.5
2		96 (88)		100	5
3		30 (22)		100	10
4		89 (82)		100	8.5
5		100 (84)		84[c]	7
6		94 (87)		100	6.5
7		65 (57)		100	9
8		43		100	10
9		40		100	5
10		93		82[d]	10
11		88		76[d]	9.5

[a] The molar ratio of substrate/NHPI/catalyst was 1000 : 50 : 7.5. The reactions were run under continues stream of O_2 (5–7 ml min^{-1}) in CH_3CN (2 ml) at 65 °C. [b] The products were identified by ^1H NMR or by comparison with authentic samples retention times of GC analysis. [c] The remainder is the related α,β-unsaturated ketone. [d] The remainder is the related epoxide.

MoO_3,[26] m-ZrO_2,[27] γ-Fe_2O_3 and TiO_2, as well as and their nanocomposites such as CoL_2@MoO_3, CoL_2@SMNP and SMNP the CoL_2@TiO_2 nanocomposite, prolonged the oxidation of norbornene under the same conditions (Fig. 2).

So, we inferred that, the catalytic activity of CoL_2@TiO_2 nanohybrid may be attributed to oxidation activity of Co(II) centers[5–9] combined with photocatalytic activity of TiO_2 core which also acts as support.[22]

To confirm of photocatalytic property of TiO_2 at the core of title nanohybrid, the aerobic oxidation of norbornene in the presence of NHPI (5 mol%) at 65 °C under UV and visible light as well as in dark were investigated after 3 and 5 h. Accelerated reactions under light radiation particularly UV light proved the photocatalytic effect of TiO_2 core on the oxidation efficiency of CoL_2@TiO_2 nanocomposite (Fig. 3). The smaller band-gap of CoL_2@TiO_2 nanohybrid (2.9 eV) than that of TiO_2 nanoparticles (3.2 eV)[22] may be a good reason for such an activity.

To establish the general applicability of the method, various olefins were subjected to the oxidation protocol under the optimized conditions (Table 1). Table 1 showed the several useful features of this catalytic method. The present oxidation method selectively produced the corresponding epoxides of norbornene, α-methylstyrene, 1-phenylcyclohexene and indene (Table 1, entries 1–4). The forming of norbornene oxide exclusively as an *exo*-isomer declared stereoselectivity of the method (entry 2). The oxidation of 1-phenylcyclohexene (entry 3) proceeded slowly demonstrating the steric effect around the active site of the catalyst is dominant.

When cyclooctene was subjected to the oxidation procedure, cyclooctene oxide was formed in 84% yield along with 16% of the related α,β-unsaturated ketone resulting from allylic oxidation (entry 5). Allylic oxidation pathway was dominant in the oxidation of cylohexene, and 2-cylohexen-1-one was appeared as sole product (entry 6). Accordingly, cyclic allylic alcohol, 2-cyclohexene-1-ol oxidized easily to the related α,β-unsaturated ketone (entry 7).

Contrary to other olefins, a terminal C=C bond conjugated with phenyl rings mainly gave the related carbonyl compounds (entries 10, 11). It seems that benzaldehyde and acetophenone are favorably formed at high temperature in the oxidation of styrene and α-methylstyrene, respectively, because high temperature will supply enough energy to break the C=C bond.[28–30]

The chemoselectivity of the procedure was notable. The linear allylic alcohols (entries 8, 9) converted selectively to the corresponding epoxides in moderate yield and no product resulting from oxidation of hydroxyl group was detected.

It should be noted that no activity was observed for 1-octene as a less reactive linear terminal olefin.

To assess the stability of catalyst during the epoxidation process, the catalyst was recovered efficiently over at least five times in aerobic epoxidation of norbornene under condition used (Fig. 4). The leaching of the catalyst was screened by centrifuging and decantation of the reaction mixture. No catalytic activity was observed in the filtrate solution and based on ICP-AES results, amount of Co in the catalyst after recycle are comparable with the fresh catalyst.

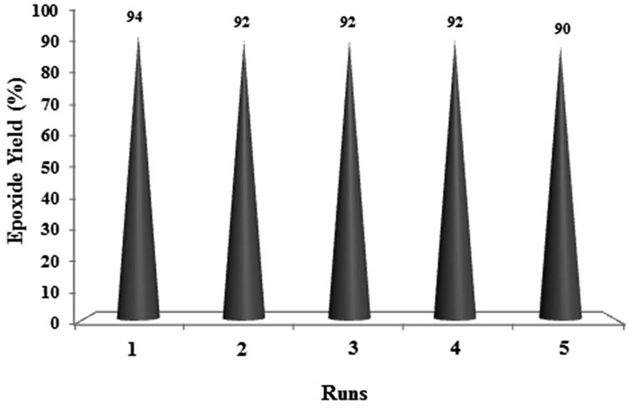


Fig. 4 Recycling of the catalytic system for oxidation of norbornene under conditions mentioned in this study.

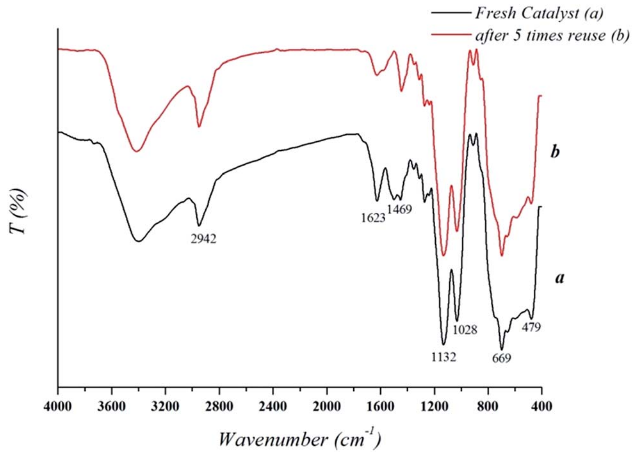


Fig. 5 The FT-IR spectra of fresh (a) and reused (b) CoL_2@TiO_2 nanocatalyst.

The FT-IR spectrum of a fresh and a reused sample of the catalyst did not show any significant differences, suggesting that the CoL_2@TiO_2 nanohybrid remained in its initial state (Fig. 5).

To demonstrate the practical utility of this method, a larger scale oxidation of norbornene (20.0 mmol) in the presence of CoL_2@TiO_2 was performed, giving norbornene oxide in 92% yield within 4 h.

3. Conclusions

In this work, we improved TiO_2 visible light photocatalytic properties by immobilizing of cobalt Schiff base complex on nanocrystalline TiO_2 for aerobic oxidation of various olefins. A synergistic effect of cobalt Schiff base complex and TiO_2 nanoparticles on the visible-light photocatalytic activity was explored. These favorable characteristics, plus the facile and efficient reusability of the solid catalyst, are the strengths of the presented work providing the scalability of the methods. Thus, our method possesses high generality which makes it suitable for industrial goals.

Acknowledgements

Support for this work by Research Council of University of Birjand is highly appreciated. We also thank "Iran Science Elites Federation" for Partial support of this work.

References

1 G.-J. Ten Brink, I. W. Arends and R. A. Sheldon, *Science*, 2000, **287**(5458), 1636–1639.

2 R. A. Sheldon, *Chem. Soc. Rev.*, 2012, **41**(4), 1437–1451.

3 M. Shibuya, Y. Osada, Y. Sasano, M. Tomizawa and Y. Iwabuchi, *J. Am. Chem. Soc.*, 2011, **133**(17), 6497–6500.

4 A. F. Lee, C. V. Ellis, J. N. Naughton, M. A. Newton, C. M. Parlett and K. Wilson, *J. Am. Chem. Soc.*, 2011, **133**(15), 5724–5727.

5 M. J. Beier, W. Kleist, M. T. Wharmby, R. Kissner, B. Kimmerle, P. A. Wright, J. D. Grunwaldt and A. Baiker, *Chem.–Eur. J.*, 2012, **18**(3), 887–898.

6 J. Gao, L. Bai, Q. Zhang, Y. Li, G. Rakesh, J.-M. Lee, Y. Yang and Q. Zhang, *Dalton Trans.*, 2014, **43**(6), 2559–2565.

7 X. Wang, S. Wu, Z. Li, X. Yang, H. Su, J. Hu, Q. Huo, J. Guan and Q. Kan, *Microporous Mesoporous Mater.*, 2016, **221**, 58–66.

8 D. Zhou, B. Tang, X.-H. Lu, X.-L. Wei, K. Li and Q.-H. Xia, *Catal. Commun.*, 2014, **45**, 124–128.

9 G. Yu, J. Sun, F. Muhammad, P. Wang and G. Zhu, *RSC Adv.*, 2014, **4**(73), 38804–38811.

10 M. K. Lajunen, *J. Mol. Catal. A: Chem.*, 2001, **169**(1), 33–40.

11 J. Jiang, K. Ma, Y. Zheng, S. Cai, R. Li and J. Ma, *Appl. Clay Sci.*, 2009, **45**(3), 117–122.

12 K. M. Jinka, S. M. Pai, B. L. Newalkar, N. V. Choudary and R. V. Jasra, *Catal. Commun.*, 2010, **11**(7), 638–642.

13 Z. Li, S. Wu, H. Ding, D. Zheng, J. Hu, X. Wang, Q. Huo, J. Guan and Q. Kan, *New J. Chem.*, 2013, **37**(5), 1561–1568.

14 N. Maksimchuk, M. Melgunov, Y. A. Chesalov, J. Mrowiec-Białoń, A. Jarzębski and O. Kholdeeva, *J. Catal.*, 2007, **246**(2), 241–248.

15 M. V. Patil, M. K. Yadav and R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2007, **277**(1), 72–80.

16 G. Xu, Q.-H. Xia, X.-H. Lu, Q. Zhang and H.-J. Zhan, *J. Mol. Catal. A: Chem.*, 2007, **266**(1), 180–187.

17 Q. Tang, Y. Wang, J. Liang, P. Wang, Q. Zhang and H. Wan, *Chem. Commun.*, 2004, 440–441.

18 H. Cui, Y. Zhang, Z. Qiu, L. Zhao and Y. Zhu, *Appl. Catal., B*, 2010, **101**(1), 45–53.

19 X.-L. Wei, X.-H. Lu, X.-T. Ma, C. Peng, H.-Z. Jiang, D. Zhou and Q.-H. Xia, *Catal. Commun.*, 2015, **61**, 48–52.

20 J. Sun, G. Yu, L. Liu, Z. Li, Q. Kan, Q. Huo and J. Guan, *Catal. Sci. Technol.*, 2014, **4**(5), 1246–1252.

21 M. Jafarpour, A. Rezaeifard, V. Yasinzadeh and H. Kargar, *RSC Adv.*, 2015, **5**(48), 38460–38469.

22 M. Jafarpour, H. Kargar and A. Rezaeifard, *RSC Adv.*, 2016, **6**(30), 25034–25046.

23 A. Rezaeifard, R. Haddad, M. Jafarpour and M. Hakimi, *J. Am. Chem. Soc.*, 2013, **135**(27), 10036–10039.

24 A. Rezaeifard, R. Haddad, M. Jafarpour and M. Hakimi, *ACS Sustainable Chem. Eng.*, 2014, **2**(4), 942–950.

25 F. Recupero and C. Punta, *Chem. Rev.*, 2007, **107**(9), 3800–3842.

26 M. Jafarpour, A. Rezaeifard, M. Ghahramaninezhad and T. Tabibi, *New J. Chem.*, 2013, **37**(7), 2087–2095.

27 M. Jafarpour, E. Rezapour, M. Ghahramaninezhad and A. Rezaeifard, *New J. Chem.*, 2014, **38**(2), 676–682.

28 R. Lin, F. Chen and N. Jiao, *Org. Lett.*, 2012, **14**(16), 4158–4161.

29 B. Tyagi, U. Sharma and R. V. Jasra, *Appl. Catal., A*, 2011, **408**(1), 171–177.

30 X. Meng, Z. Sun, R. Wang, S. Lin, J. Sun, M. Yang, K. Lin, D. Jiang and F.-S. Xiao, *Catal. Lett.*, 2001, **76**(1–2), 105–109.