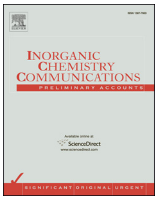
Inorganic Chemistry Communications 46 (2014) 198–201

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche



Cooperative catalysis by polymetallic copper–zinc complexes in the efficient oxidation of alcohols under solvent free condition

Rosmita Borthakur [a], Mrityunjaya Asthana [b], Arvind Kumar [c], Ram A. Lal [a,*]

[a] Department of Chemistry, Centre for Advance Studies in Chemistry, North Eastern Hill University, Shillong 793022, Meghalaya, India
[b] Departement of Chemistry, Centre of Advanced Study, Banaras Hindu University, Varanasi 221005, India
[c] Department of Chemistry, Faculty of Science and Agriculture, The University of West-Indies, St. Augustine, Trinidad and Tobago

ARTICLE INFO

Article history:
Received 24 March 2014
Accepted 8 May 2014
Available online 25 May 2014

Keywords:
Cooperative catalysis
Polymetallic complexes
Oxidation
Alcohols
Carbonyl compounds

ABSTRACT

The oxidation of alcohols to corresponding aldehydes and ketones has been achieved using polymetallic complexes as catalyst with hydrogen peroxide as the terminal oxidant under a solvent free condition. These polymetallic complexes linked to a single ligand system exhibited remarkable cooperative effect in the oxidation process. This ecologically friendly procedure releases water as the only by-product.

Catalytic oxidation is a key technology to transform alcohols into carbonyl compounds. In the current chemical industries noble metal catalysts are used on a large scale. Due to limited resources of noble metals chemists are prompted to develop new-generation catalysts in which noble metal contents are effectively reduced [1]. In this regard, the first transition metal polymetallic complexes often exhibit an enhancement of catalytic activity and selectivity compared with their monometallic counterparts [2–4] and have the potential to be new-generation catalysts by partially or even completely replacing noble metals with non-noble metals. Mononuclear metal complexes have received great attention but the adventure of hetero-metal complexes comes from reactivity hitherto unseen in their mono/homo dinuclear counterparts.

Combining multiple catalytic sites into a single ligand structure can induce cooperative reaction pathways, improving the activities and selectivities. Research groups are developing polymetallic catalytic systems to find synergy and cooperative effects between different metal centers for activation of reagents and better results [5]. Hydrazones are a special kind of polyfunctional Schiff base ligands which have the potential for yielding homo- and hetero-metallic complexes among which succinoyldihydrazones are unique because of their greater flexibility [6].

Heterogeneous catalysts are desirable from both economic and industrial viewpoints because of the reusability of the catalysts and the easy purification of the products as compared to homogeneous catalysts.

From both an economic and environmental point of view, the quest for effective catalytic oxidation processes that use clean, inexpensive primary oxidants, such as molecular oxygen or hydrogen peroxide, i.e., a "green method" for converting alcohols to carbonyl compounds on an industrial scale, remains an important challenge [7]. In this communication, we report heterogeneous catalytic systems of poly-metallic complexes linked to a single ligand scaffold (Fig. 1) [8–10], exhibiting remarkable catalytic cooperative effects in the selective oxidation of alcohols to carbonyl compounds using H_2O_2 as a terminal oxidant. The contribution is organized according to the donor centers of the ligand to which the metal centers are bonded [2]. These polymetallic complexes have been selected keeping in view the fact that bis(5-bromosalicyaldimine)succinoyldihydrazone is bulkier than bis(2-hydroxynaphthaldimine)succinoyldihydrazone. Such special features associated with the structures of the ligand are expected to play significant roles in the catalytic activity of the catalyst.

Continuing our interest in exploring the catalytic properties of our synthesized complexes [11] we report, herein a very efficient and selective oxidation of alcohols with H_2O_2 using reusable heterogeneous catalysts under solvent-free condition. The present protocol is very simple, mild and environment friendly with water being the only by-product in the reaction. No over oxidation of the alcohols to the acids occurred (Scheme 1).

---

* Corresponding author. Tel.: +91 0364 2722616; fax: +91 364 2550486.
E-mail address: profralal@gmail.com (R.A. Lal).

http://dx.doi.org/10.1016/j.inoche.2014.05.018
1387-7003/© 2014 Elsevier B.V. All rights reserved.

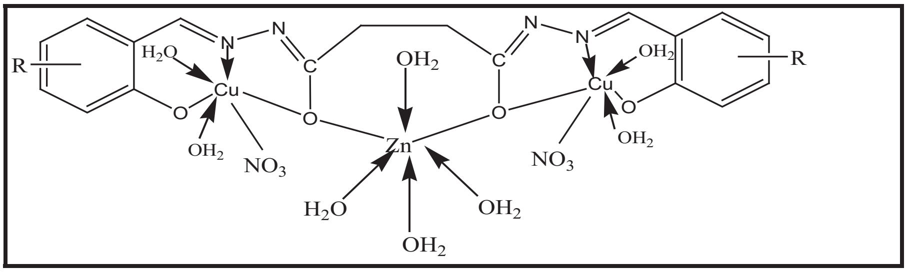
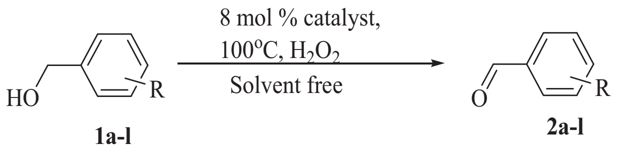


Fig. 1. The structure of $[ZnCu_2(H_4L^n)(NO_3)_2(H_2O)_8]{\cdot}2H_2O$ ($H_4L^n = H_4L^1(1), H_4L^2(2)$). (R = 2-hydroxy-1-naphthaldehyde and Br, respectively).

The detail of preparation and characterization of catalysts [12] $[ZnCu_2(L^n)(NO_3)_2(H_2O)_8]{\cdot}2H_2O$ where ($H_4L^n = H_4L^1$ (**1**), H_4L^2 (**2**)) has been reported in our earlier publication [8].

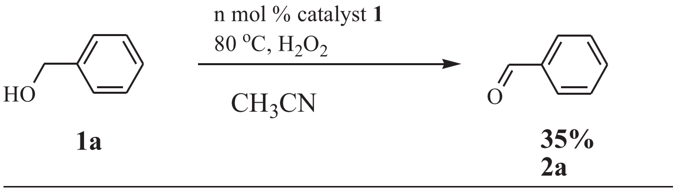
The catalytic efficiency of the synthesized trinuclear complexes **1–2** were explored for the oxidation of alcohols to corresponding carbonyl compounds [13]. Our initial experiments were performed on benzyl alcohol with H_2O_2 using complex **1** in acetonitrile under reflux to find the best reaction conditions. The results are shown in (Table 1).

It was found that high conversion and good yield of oxidation product were obtained by employing 8 mol% of catalyst **1** (Table 1, entry 3). The synthetic transformation did not proceed in the absence of catalyst (entry 6). This observation revealed the catalytic role of the complex. It was observed that the oxidation of benzyl alcohol to the corresponding benzaldehyde did not proceed at all when the monometallic copper [14] and zinc [15] complexes were used as catalyst (entries 7–10). This result showed that two metal centers are better than one metal center and work in better harmony with one another, thus exhibiting cooperative effect of one another. Encouraged by these results, we screened different solvents for the oxidation of **1a** using catalyst **1** under the reflux condition and also under the solvent free condition. Results are summarized in (Fig. 2). Except for CH_3CN all other solvents gave very low yields of **2a**. The oxidation of **1a** under the solvent free condition gave the best yield of **2a**.



Scheme 1. Oxidation of alcohol using catalyst.

Table 1
Amount of catalyst variation of **1** for oxidation of benzyl alcohol.



Entry	Catalyst **1** (in mol%)	Time (h)	Yield (%)[a]
1[b]	2%	36	15
2[c]	5%	16	35
3[d]	8%	12	40
4[e]	10%	16	30
5[f]	15%	20	25
6[g]	–	24	–
7[h]	5%	24	–
8[i]	5%	24	–
9[h]	8%	24	–
10[i]	8%	24	–

a Isolated yields.

b Reaction conditions: substrate (5 mmol), catalyst (2 mol%[b], 5 mol%[c], 8 mol%[d], 10 mol%[e], 15 mol%[f], no catalyst[g], $[Cu(H_2L)(H_2O)]$[h] and $[Zn(H_2L)(H_2O)_2]$[i]), H_2O_2, CH_3CN (3 mL), 80 °C (oil bath temperature).

Thus, our optimized reaction conditions are **1a** (5 mmol), H_2O_2 and 8 mol% of catalyst under a solvent free condition. The oxidation of other primary, secondary, allylic and aliphatic alcohols were then examined using the optimized protocol. Complex **2** was also found to catalyze the oxidation of alcohols to corresponding carbonyl compounds under the solvent free condition in 60–82%. Catalyst **1** showed better results than catalyst **2**. This may be due to the fact that the catalytic activity of complexes varies with the size of the substituent. It was observed that the activity decreases with an increase in the bulkiness of the substituent. This may be due to the steric hindrance caused by the substituent, which can affect the planarity of the ligand in the complexes and hence the approach of the incoming substrate to the center. The results for the oxidation of a variety of alcohols are summarized in Table 2. All the reactions occurred in open atmosphere with complete selectivity for ketones or aldehydes and no other product was detected in the reaction mixture. So, it is clear that air is not a significant co-oxidant in the oxidation process and copper (II) complexes are air stable.

It is also important to verify the viability of reusing catalytic system for different substrates. The basic advantage of heterogeneous catalyst is their reuse for consecutive catalytic cycles. To evaluate the catalyst reusability, it was recovered by filtration, washed with DCM and dried in the oven for 30 min. Catalyst was reused under the optimized condition with benzyl alcohol to give the corresponding benzaldehyde; the data obtained are shown in (Fig. 3).

In conclusion, we have developed an efficient heterogeneous catalytic system based on Cu(II)–Zn(II), showing cooperative effect for the oxidation of benzylic, allylic and aliphatic alcohols to the corresponding carbonyl compounds using hydrogen peroxide as an oxidant under solvent free condition. Furthermore, the catalyst can be recovered and

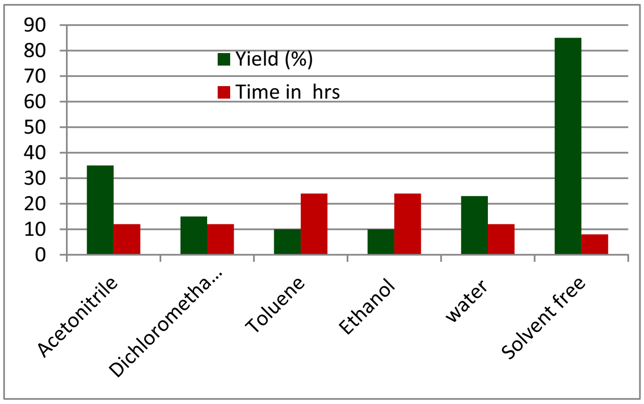
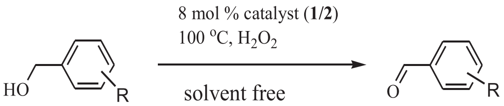
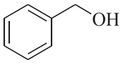
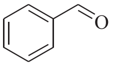
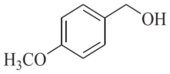
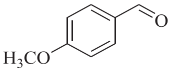
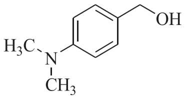
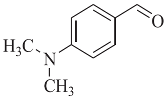
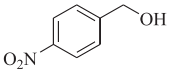
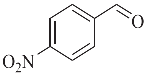
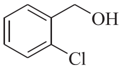
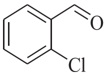
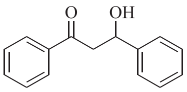
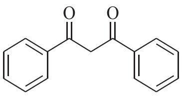
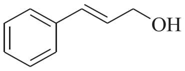
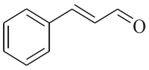
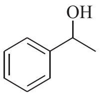
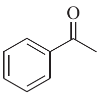
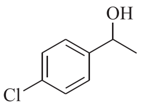
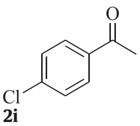
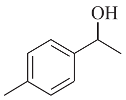
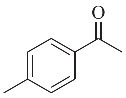
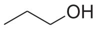
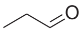
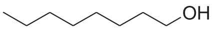
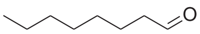


Fig. 2. Optimization of solvent effect.

Table 2
Oxidation of alcohols catalyzed by Cu(II)–Zn(II) complexes **1** and **2**[a].



Entry	Substrate	Product	**1** yield (%)[b] time (h)	**2** yield (%)[b] time (h)
1	 **1a**	 **2a**	84% 12 h	81% 14 h
2	 **1b**	 **2b**	86% 12 h	82% 15 h
3	 **1c**	 **2c**	82% 11 h	80% 14 h
4	 **1d**	 **2d**	80% 11 h	77% 16 h
5	 **1e**	 **2e**	76% 12 h	72% 16 h
6	 **1f**	 **2f**	80% 14 h	76% 16 h
7	 **1g**	 **2g**	81% 12 h	78% 14 h
8	 **1h**	 **2h**	78% 14 h	75% 17 h
9	 **1i**	 **2i**	75% 17 h	70% 20 h
10	 **1j**	 **2j**	79% 14 h	75% 18 h
11	 **1k**	 **2k**	70% 22 h	67% 27 h
12	 **1l**	 **2l**	65% 30 h	60% 35 h

[a] Reaction condition: substrate (5 mmol), catalyst **1**/**2** (8 mol%), H_2O_2 was heated at 100 °C for appropriate time.
[b] Isolated yields.

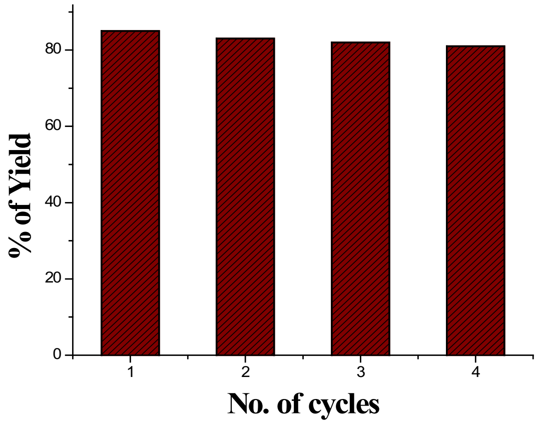


Fig. 3. Reusability chart of catalyst.

reused without any significant loss of catalytic activity. The catalytic system derived from more sterically crowded polyfunctional ligand is less reactive than that derived from less sterically crowded ligand.

Acknowledgments

Authors are thankful to Head, SAIF, North Eastern Hill University, Shillong for elemental analyses and recording spectra. RB would like to thank UGC, New Delhi for the award of RFSMS and MA to CSIR, New Delhi for the award of Senior Research Fellowship.

Appendix A. Supplementary material

Spectral data of the compounds are provided in the SI file. This material is available free of charge via the Internet. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.05.018. These data include MOL files and InChiKeys of the most important compounds described in this article.

References

[1] J. Lin, J. Chen, W. Sua, Adv. Synth. Catal. 355 (2013) 41–46.
[2] I. Bratko, M. Gómez, Dalton Trans. 42 (2013) 10664–10681.
[3] J.M. Ready, E.N. Jacobsen, Angew. Chem. Int. Ed. 41 (2002) 1374–1377.
[4] M.L. Kantama, R.S. Reddya, U. Pala, M. Sudhakara, A. Venugopala, K.J. Ratnama, F. Figuerasb, V.R. Chintareddy, Y. Nishinad, J. Mol. Catal. A Chem. 359 (2012) 1–7.
[5] (a) E.K. Beuken, B.L. Feringa, Tetrahedron 54 (1998) 12985–13011;
(b) M. Shibasaki, N. Yoshikawa, Chem. Rev. 102 (2002) 2187–2209;
(c) J.I. van der Vlugt, Eur. J. Inorg. Chem. (2012) 363–375;
(d) J. Park, S. Hong, Chem. Soc. Rev. 41 (2012) 6931–6943;
(e) K.-H. Wu, H.-M. Gau, J. Am. Chem. Soc. 128 (2006) 14808–14809.
[6] (a) M. Sutradhar, T.R. Barman, J. Klanke, M.G.B. Drew, E. Rentschler, Polyhedron 53 (2013) 48–55;
(b) R.A. Lal, D. Basumatary, A. Adhikari, A. Kumar, Spectrochim. Acta A 69 (2008) 706–714;
(c) A. Kumar, R. Borthakur, A. Koch, O.B. Chanu, S. Choudhury, A. Lemtur, R.A. Lal, J. Mol. Struct. 999 (2011) 89–97;
(d) M. Sutradhar, T.R. Barman, G. Mukherjee, M.G. Drew, S. Ghosh, Polyhedron 34 (2012) 92–101;
(e) R.A. Lal, S. Choudhury, A. Ahmed, R. Borthakur, M. Asthana, A. Kumar, Spectrochim. Acta A 75 (2010) 212–224.
[7] A. Dijksman, A. M.-Gonza'lez, A. M. i Payeras, I. W. C. E. Arends, R. A. Sheldon, J. Am. Chem. Soc. 123 (2001) 6826–6833.
[8] R. Borthakur, A. Kumar, R.A. Lal, J. Ind. Chem. Soc. 9 (2014) 407–423.
[9] R. Borthakur, A. Kumar, A. Lemtur, R.A. Lal, RSC Adv. 3 (2013) 15139–15147.
[10] R. Borthakur, A. Kumar, R.A. Lal, Spectrochim. Acta A 118 (2014) 94–101.
[11] (a) R. Borthakur, M. Asthana, A. Kumar, A. Koch, R.A. Lal, RSC Adv. 3 (2013) 22957–22962;
(b) R. Borthakur, M. Asthana, M. Saha, A. Kumar, A.K. Pal, RSC Adv. 4 (2014) 21638–21643.
[12] (a) All the reagents used were chemically pure and were of analytical reagent grade. 4-nitro benzyl alcohol and 4-methoxy benzyl alcohol were purchased from Aldrich and the rest of the chemicals along with solvent were procured from local suppliers. The solvents were dried and distilled before use following the standard procedures.[12] Melting points were recorded in open capillaries and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in CDCl3 on a Bruker Avance-400 spectrometer and Jeol-300 and 500 spectrometer.
(b) A.I. Vogel, Textbook of Practical Organic Chemistry, 5th ed. Longman, London, 1989.
[13] All of the reactions were carried out at 100 °C under reflux in a 25 mL flask equipped with a magnetic stirrer. 30% H_2O_2 solution was added to a mixture of alcohol (5 mmol) and the catalyst (8 mol%). The reaction solutions in all cases were vigorously stirred using magnetic stirrers, and an oil bath was used to achieve the desired reaction temperature. After completion (TLC), the reaction mixture was cooled to room temperature and filtered. Filtrate was extracted with ethylacetate (3 × 10 mL) and the

combined organic extract was washed with water (3 × 10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified by column chromatography over silica gel (60–120 mesh) using ethyl acetate and hexane as eluent to afford the pure products **2a**–**l**.

[14] R. Borthakur, A. Kumar, A.K. De, R.A. Lal, Arab. J. Chem. (2014) (Revision submitted for publication).
[15] R.A. Lal, M. Chakraborty, O.B. Chanu, S. Choudhury, R. Borthakur, S. Copperfield, A. Kumar, J. Coord. Chem. 63 (2010) 1239–1251.