



Application of Copper(II) Schiff Base Complex Grafted in the Silica Network as Efficient Nanocatalyst in Oxidation of Alcohols

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Bis[*S*-allyl- β -N-(benzylidene)dithiocarbazato]copper(II) complex was grafted into SiO₂ matrix. Heterogenized catalyst was characterized by FT-IR, SEM, EDX TEM, N₂ absorption and atomic absorption spectroscopy (AAS) and its catalytic performance in the oxidation of alcohols was investigated. The experimental results showed that the prepared heterogeneous nanocatalyst is an efficient and selective catalyst for examined oxidation reaction. Thus, secondary alcohols were oxidized to ketones and primary alcohols converted to aldehydes by hydrogen peroxide in the presence of newly nanocatalyst in mild conditions.

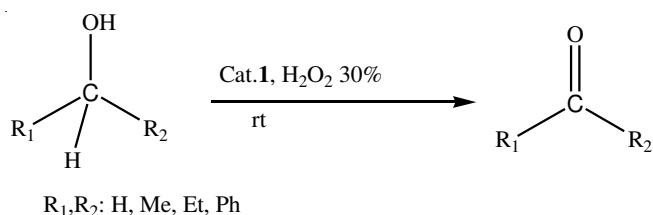
Key Words: Alcohols oxidation, Grafted copper Schiff base complex, Aldehyde, Hydrogen peroxide, Nanocatalyst.

INTRODUCTION

Homogeneous metal Schiff base complexes bearing NS macrocyclic ligands have attracted much interest in the field of catalysis because of their reversible oxygen bonding ability and high activities in oxidation reactions¹⁻⁷. However, the homogeneous catalysts have some drawbacks such as problems in the catalyst recovery and product separation. In addition, as far as pharmaceutical product is concerned, potential contamination of metal catalyst, which is specifically undesirable in the cases of homogeneous catalysis, has to be carefully considered. Furthermore, the use of metal Schiff base complexes as catalyst in homogeneous solution often suffers from deactivation due to easy formation of dimeric peroxo and μ -oxo species, which have been demonstrated to be inactive in different catalytic reactions⁸⁻¹⁰.

In order to overcome these drawbacks, heterogenization of homogeneous catalysts with comparable activities affords an appealing methodology to expand the industrial application of homogeneous catalysts. For this reason, immobilization of metal Schiff base complexes on organic or inorganic polymers and inorganic supports has been widely reported^{11,12}. A variety of copper(II) salts is suitable as catalysts or catalyst precursors¹³. In particular, Schiff base complexes of copper(II) have been used as catalysts in the aziridination and cyclopropanation of olefins and also in phenol oxidation¹⁴⁻¹⁸. The heterogenization of transition metal complexes is an area of growing interest, particularly on zeolites, mesoporous silicate materials, polymers and activated carbon¹⁹⁻²⁷. Recently, several

salen complexes have been immobilized on activated carbon²¹ and sol-gel²⁸. However, either leaching or mean selectivity was the main problem during their application as catalysts. Karandikar *et al.*²⁹ have grafted copper and cobalt salen compounds on the surface of MCM-41 through aminosilane linker by adduct formation. The metal Schiff base complexes as catalyst were found to be active for epoxidation reactions. The stability of the complexes on the surface and the recyclability of the catalysts, however, were not examined²⁹. H₂O₂ has also merged as popular oxidant in the past decade³⁰. In the present study, we have heterogenized copper(II) Schiff base complex (Fig. 1) on the surface of gelatine/siloxane hybrid prepared *via* sol-gel method as nanocatalyst. The test of catalytic activity of the grafted Schiff base complex, catalyst (**1**) was carried out with various alcohols in the presence of H₂O₂ as oxidant. All products characterized by ¹H NMR and IR spectroscopy. In this work, we present an efficient method for the catalytic oxidation of primary and secondary alcohols to corresponding carbonyl compounds using H₂O₂ as an oxidant over catalyst (**1**) (Scheme-1).



Scheme-I

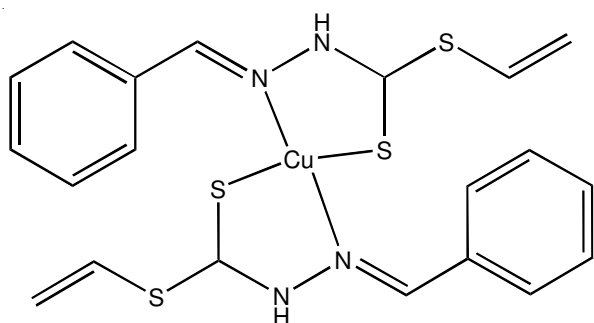


Fig. 1. Bis[S-allyl-β-N-(benzylidene)dithiocarbazato]-copper(II) complex

EXPERIMENTAL

Bis[S-allyl-β-N-(benzylidene)dithiocarbazato]-copper(II) complex (Fig. 1) was prepared according to literature procedure³¹. Alcohols were obtained from Aldrich company and tetraethyl orthosilicate (TEOS) was obtained from Merck company. All materials were used as received without purification. All the isolated disulfide compounds were identified through ¹H NMR.

Preparation of bis[S-allyl-β-N-(benzylidene)dithiocarbazato]copper(II) complex: Preparation of the complex is straightforward and is analogous to the procedure described³¹, copper(II) nitrate trihydrate (0.242 g; 0.001 mol) in ethanol (10 mL) was added to the ethanolic solution of ligand S-allyl-β-N-(benzylidene)dithiocarbazate (0.473 g; 0.002 mol). The mixture was heated and then left to stand overnight. The product was filtered off, washed with ethanol, dried in a vacuum. Yield 69 % (Fig. 1).

Preparation of gelatine/silica composite: The gelatine/silica was prepared using tetraethyl orthosilicate (TEOS, 99 %, Aldrich), as the silica source, gelatine as organic source, ethanol (EtOH) as solvent, distilled water and HCl, the precursor solution was prepared as follows: one mole TEOS was mixed with 4 mol of ethanol, 4 mol of distilled water and stirred for ca. 0.5 h, 0.01 mol hydrochloric acid (HCl, 37 wt % in water) was added into the solution and then the solution was stirred at room temperature for 1 h. For the organic component 12 wt % gelatine solution previously prepared at 45 °C with magnetic stirring for ca. 2 h, mixed together and stirred for 24 h. The xerogel was dried at 70 °C for 20 h and then calcinated at 750 °C for 7 h, the temperature and time predetermined for a specific experiment, with a temperature gradient 10 °C/min.

Preparation of heterogenized Cu(II) Schiff base complex, catalyst (1): Silica composite was activated by refluxing in concentrated hydrochloric acid and then washed thoroughly with deionized water and dried before undergoing chemical surface modification. Hydrated silica was then added to Schiff base complex solution and the mixture was stirred over night. The solvent was removed using a rotary evaporator and the resulting olive green solid dried at 80 °C overnight. The product was washed with MeOH and water until the washings were colourless. Further drying of solid product was carried out in an oven at 80 °C for 8 h.

Catalytic reaction: The catalytic reaction was undertaken in a glass batch. Oxidation of alcohols was performed at room temperature in the presence of catalytic amount of the catalyst (1) using hydrogen peroxide as the oxidant. The oxidation of benzhydrol and benzyl alcohol as model substrate carried out for optimization of the reaction variables such as temperature, H₂O₂/alcohol molar ratio, appropriate amount of catalyst and length of the reaction time. A typical experimental procedure was as follows: to the catalyst (1) (0.1 mmol) was added the substrate alcohol (1 mmol), then hydrogen peroxide (10 mmol, 30 %) was slowly added. The reaction mixture was stirred at room temperature until TLC pointed out the reaction was complete. The catalyst was separated by a simple filtration and product was obtained in high purity after evaporation of solvent. Oxidation took place to afford benzophenone in the presence of catalyst and H₂O₂ (10 eq, 30 %) in 55 min (Table-1, entry 1). Perhaps some of hydrogen peroxide was decomposed in the presence of catalyst (1) and O₂ was released in the course of reaction. Determine which of H₂O₂ or released O₂ plays essential role in the oxidation reaction in the presence of our catalyst. We examined this reaction by simply bubbling molecular oxygen through reaction mixture under similar conditions and only a poor yield of product was obtained (Table-1, entry 2). So, decomposition played little role in the oxidation of alcohols. Furthermore, when the oxidation of benzhydrol was carried out using less catalyst, the reaction was found to reach completion over much longer time (Table-1, entry 3). When the silica matrix was used, as catalyst, no reaction took place and the starting materials were recovered (Table-1, entry 4). Alternatively, the reaction was carried out at 50 °C under the same conditions in which, the oxidation completed after 0.5 h (Table-1, entry 5). Oxidation of benzyl

TABLE-1
OPTIMIZATION OF REACTION CONDITIONS BY OXIDATION OF BENZHYDROL IN CH₂Cl₂ AT ROOM TEMPERATURE^a

Entry	Substrate	Product	Oxidant	Temp. (°C)	Catalyst (mol %)	Reaction time (min)	Conversion (%)	Selectivity
1	Benzhydrol	Benzophenone	H ₂ O ₂	25	Cat. 1 (10%)	55	100	100
2	Benzhydrol	Benzophenone	O ₂	25	Cat. 1 (10%)	55	< 20	Small
3	Benzhydrol	Benzophenone	H ₂ O ₂	25	Cat. 1 (5%)	85	100	100
4 ^b	Benzhydrol	Benzophenone	H ₂ O ₂	25	Silica composite	55	No reaction	No reaction
5	Benzhydrol	Benzophenone	H ₂ O ₂	50	Cat. 1 (10%)	30	100	100
6	Benzyl alcohol	Benzoic acid, benzaldehyde	H ₂ O ₂	25	–	70	100	20
7	Benzyl alcohol	Benzoic acid, benzaldehyde	H ₂ O ₂	25	Cu(Schiff base) complex	35	100	80
8	Benzyl alcohol	Benzaldehyde	H ₂ O ₂	25	Cat. 1 (10 %)	35	100	100

^aBenzhydrol 1mmol, room temperature, 0.1 mmol of cat. (1), 10 mmol aqueous 30 % H₂O₂. ^bThe reaction carried out with 2 g of gelatin/Silica composite.

alcohol took place in the absence of catalyst just in presence of H_2O_2 (10 eq, 30 %), the main product of this reaction was benzoic acid with a few amount of benzaldehyde (Table-1, entry 6). When we used homogeneous Schiff base complex as catalyst, benzyl alcohol conversion accelerated and selectivity was improved (Table-1, entry 7). On the other hand, in the presence of heterogeneous Schiff base catalyst, the catalytic performance effectively improved. The optimal conversion of benzyl alcohol reached to 100 % and exclusively benzaldehyde was obtained over immobilized catalyst (Table-1, entry 8).

RESULTS AND DISCUSSION

Immobilization of the copper(II) Schiff base complex:

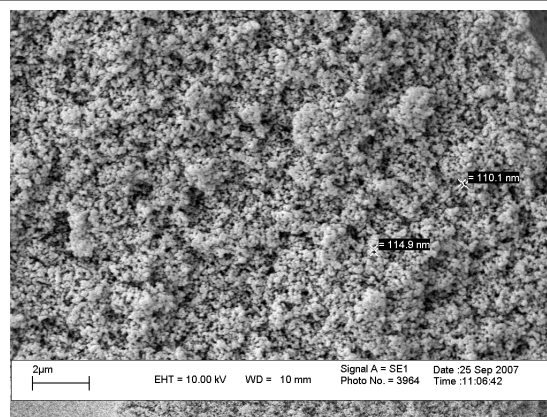
The metal complex was immobilized in silica matrix by following ship-in-a-bottle procedure³². Actually, the complex physically trapped in the cage of the porous silica network. The complex was anchored over silica matrix by refluxing for 6 h in ethanol solution and then it was extracted with ethanol in Soxhlet extractor for 6 h. The Cu content was determined by atomic absorption analysis.

IR spectroscopy: We first prepared the homogeneous catalyst Cu(II) complex as described by Yazdanbakhsh *et al.*³¹. Its structure is shown in Fig. 1. This complex was physically grafted into the SiO_2 matrix. The grafted conditions are mild, which can ensure the stability of the complex in the process. The FT-IR spectra of the neat complex and catalyst (**1**) are shown the bands at the frequencies of 1630, 1592 and 680 cm^{-1} , which are assigned to $\text{C}=\text{C}$, $\text{C}=\text{N}$ and vibration of the skeleton of the phenyl group, respectively. The reason is that the content of the complex is so low that its absorption bands are masked by the strong background bands of the SiO_2 matrix. Frequencies of 1100 and 800 cm^{-1} are assigned to stretching vibration of $\text{Si}-\text{O}-\text{Si}$ and $\text{Si}-\text{OH}$, respectively.

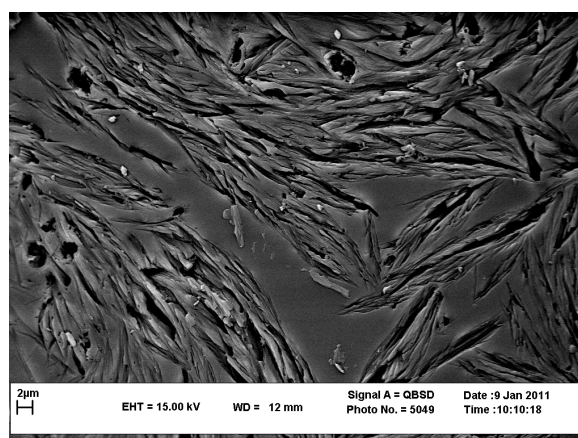
Atomic absorption spectroscopy (AAS): To confirm that the complex was indeed grafted in the matrix, AAS employed to analyze the content of Cu in the catalyst. The result showed the content of Cu is (0.19 %) because the catalyst was extracted with ethanol thoroughly, no contaminated complex on the matrix was left and the Cu content should come from the complex grafted in the matrix.

TEM, SEM test results: SEM and TEM images were used to evaluate the surface morphology and size distribution of the nickel complex deposited in the silica network. The prepared catalyst (**1**) was analyzed by TEM (Fig. 2c). The particle size of catalyst (**1**) was lower than 15 nm, which was much smaller than the nano-Silica particle size. The SEM (Fig. 2a) of the silica network shows the average diameter of 115 nm. Hence, catalyst (**1**) could be attached to the surface of the nano-Silica particle. A clear change in the morphology was occurred after the addition of Cu Schiff base complex to the support Fig. 2b. SEM showed that the number of pores for the catalyst clearly decreased and the N_2 absorption/desorption confirmed it. It is deduced that more sites will be enable to increase the catalytic activity of the nanocatalyst (**1**).

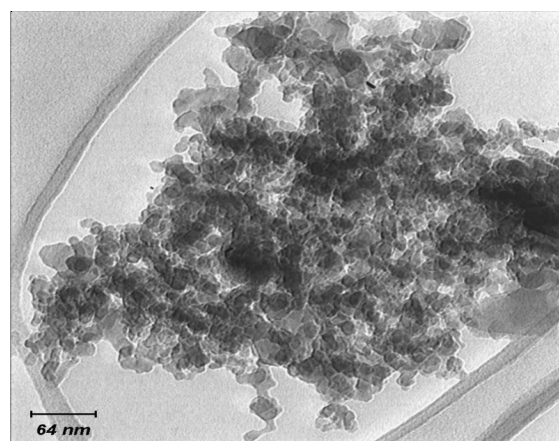
BET of substrate and catalyst: Surface analysis showed the surface area of the catalyst as $167\text{ m}^2/\text{g}$ (Fig. 3a) and the gelatine/siloxane hybrid as $433\text{ m}^2/\text{g}$ (Fig. 3b). Total pore



(a)



(b)

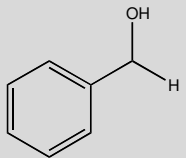
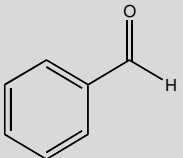
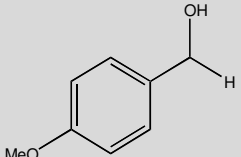
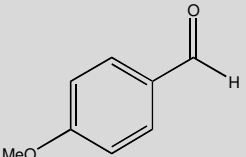
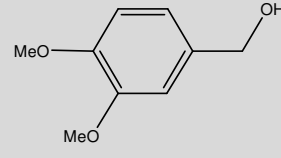
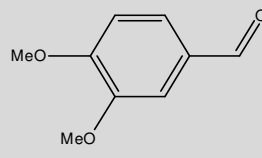
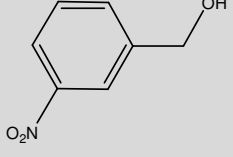
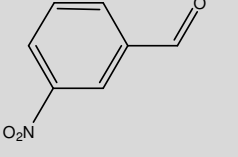
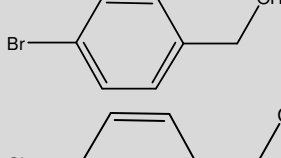
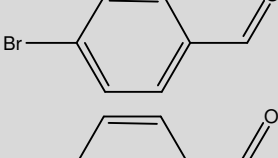
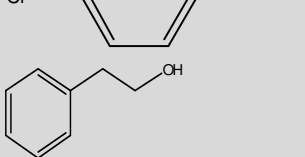
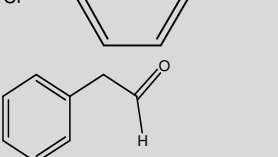
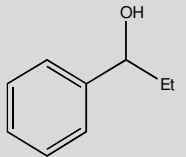
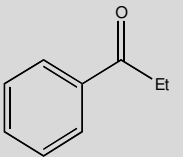
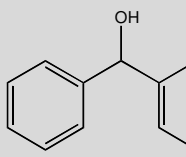
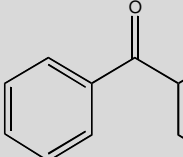
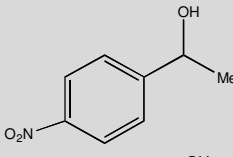
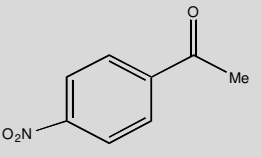
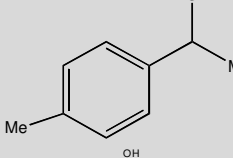
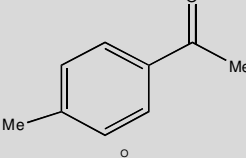
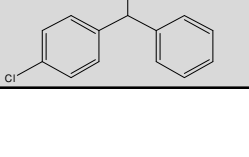
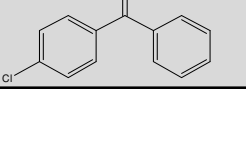


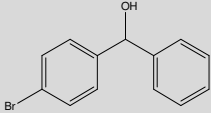
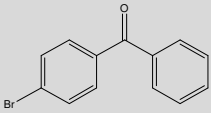
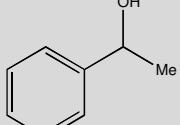
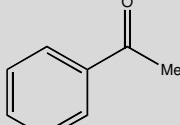
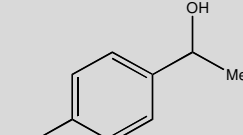
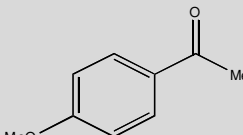
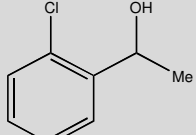
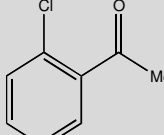
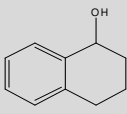
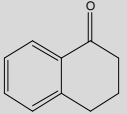
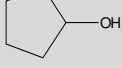
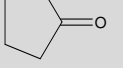
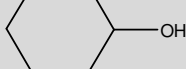
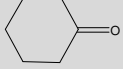
(c)

Fig. 2. (a) SEM micrograph of gelatin/siloxane composite, (b) SEM image of grafted Cu(II) Schiff base complex (c) TEM image of grafted Cu(II) Schiff base complex

volume in single point ($P/P_0 = 0.99731$) of the catalyst is $0.097\text{ cm}^3/\text{g}$ (Fig. 3a) compared to $0.231\text{ cm}^3/\text{g}$ for the support (Fig. 3b). This indicated the heterogeneous catalyst brings about a substantial reduction in surface area, possibly due to pore blockade from the gelatin/siloxane, limiting access to very strait-entrance pores in the material. Pore size of the catalyst was 17.8 \AA (Fig. 3a), as compared to 13.8 \AA for the support (Fig. 3b); this indicated the total pore volume of catalyst was reduced. The number of support pores is higher than in the catalyst, while the catalyst has a larger pore diameter.

TABLE-2
 OXIDATION OF ALCOHOLS TO CORRESPONDING CARBOXYLIC GROUP BY CATALYST (1)^a

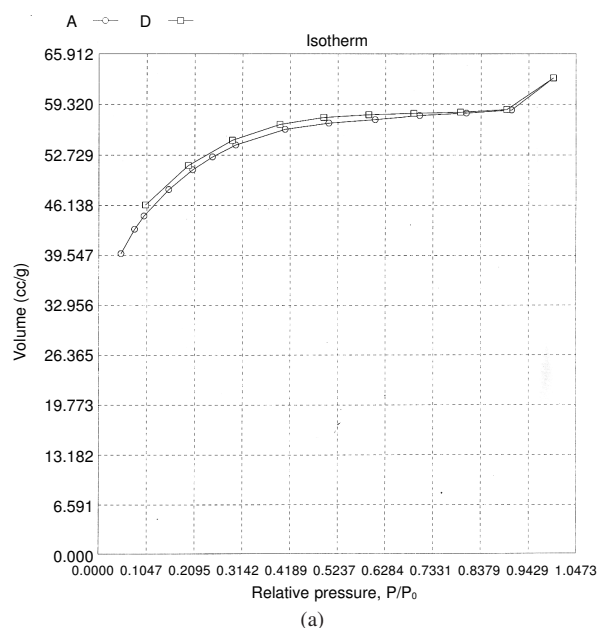
Entry	Substrate	Product	Yield (%)	Time (min)	Selectivity
1			85	35	100
2			98	30	100
3			99	25	100
4			99	45	100
5			99	35	100
6			99	35	100
7			95	80	100
8			95	65	100
9			95	55	100
10			92	95	100
11			95	60	100
12			96	65	100

13			98	65	100
14			92	70	100
15			98	55	100
16			90	65	100
17			94	110	100
18			98	150	100
19			98	240	100

Reaction condition: substrate 1 mmol, room temperature, 0.1 mmol of cat. (1), 10 mmol 30 % aqueous H₂O₂.

Catalytic reaction: The oxidation of alcohols was carried out to test the catalytic efficiency of the prepared catalyst. To show the generality and scope of this procedure, the reaction was examined with various alcohols such as primary, secondary and aliphatic alcohols, the results summarized in Table-2. Efficient oxidation was observed on the benzylic alcohols but for the oxidation of aliphatic alcohols extra times are required (Table-2, entries 17, 18). Moreover, the reaction of cyclohexanol (Table-2, entry 19), required the addition of an extra 10 mmol % of H₂O₂ after 150 min. The primary benzylic alcohols were found to be reactive and afforded selectively to their corresponding aldehydes as compared to other aliphatic primary alcohols. Secondary or benzylic or aliphatic alcohols gave corresponding ketones in high yields. The yields were confirmed after the products were isolated by filtration and purification with ethyl acetate/*n*-hexane. Although conversion was observed by TLC, typically, 5-12 % of products were lost during the work-up procedure. The Cu(II) [Schiff base]/SiO₂ also showed almost good catalytic activity in solution of oxidation reaction. Atomic absorption spectrometric analysis shows that copper is not leaching out during oxidation reactions. No copper was detected in the liquid phase of the reaction mixture, after the completion of reaction. The catalyst (1) affords selectively only aldehyde (Table-2, entries 1-7) instead of the two usual product (aldehyde and carboxylic acid) in oxidation of primary alcohols, in case of the oxidation of secondary alcohols, the catalyst (1) affords selectively only ketone instead of two possible product (ketone and carboxylic ester). After the first use of the catalyst, the reusability of the

catalyst (1) in the oxidation of benzhydrol (Table-1, entry 1) was carefully examined. The recovered catalyst was successfully used in 7 subsequent runs without any significant loss in catalytic activity under similar experimental conditions (Table-3). No pre-treatment step was used, although the recovered catalyst washed with mixed solvent of ethanol/*n*-hexane by 1:9 molar ratios to remove traces of the previous reaction mixture and dried before the next cycle.



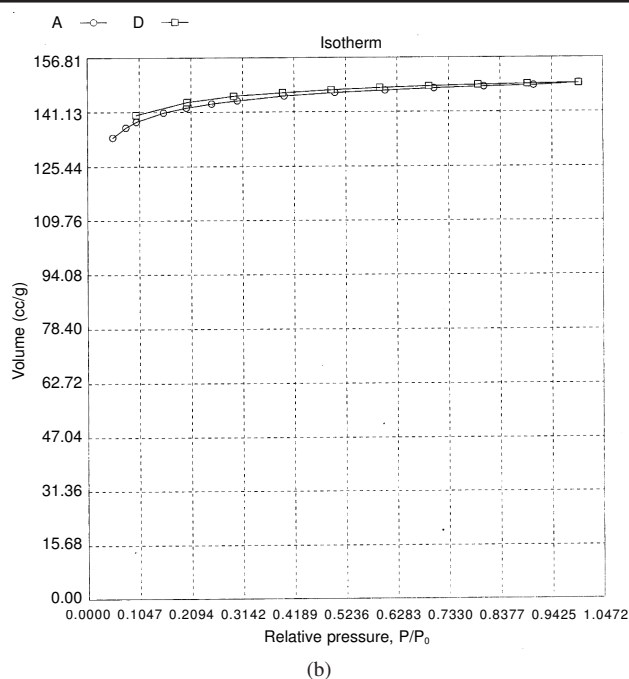


Fig. 3. (a) BET of grafted Schiff base complex, (b) BET of gelatine/siloxane composite

TABLE-3
REUSABILITY OF CATALYST (1) UNDER
THE SAME REACTION CONDITIONS^a

Run No.	1	2	3	4	5	6	7
Yield (%)	95	95	95	95	92	92	85
Time (min)	55	55	55	55	70	70	110

^aBenzhydrol 1 mmol, room temperature, 0.1 mmol of cat. (1), aqueous 30 % H₂O₂ 10 mmol.

Conclusion

In order to show the effect of grafted copper(II) Schiff base complex in the alcohols oxidation, the system was found to be selective and both cycloalkanols and benzylic alcohols were oxidized in excellent yields. Our results indicate that catalyst (1) is an effective catalyst for oxidation of alcohols by hydrogen peroxide. An important advantage of this method aside from this condition does not require a difficult way for separation of the product and catalyst. Catalyst was successfully used in 7 subsequent runs without any significant loss in catalytic activity under similar experimental conditions.

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REFERENCES

1. E.N. Jacobsen, W. Zhang and M.L. Guler, *J. Am. Chem. Soc.*, **113**, 6703 (1991).
2. E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker and L. Deng, *J. Am. Chem. Soc.*, **113**, 7063 (1991).
3. W. Zhang, J.L. Loebach, S.R. Wilson and E.N. Jacobsen, *J. Am. Chem. Soc.*, **112**, 2801 (1990).
4. S.E. Schaus, J. Branalt and E.N. Jacobsen, *J. Org. Chem.*, **63**, 403 (1998).
5. J. Lopez and S. Liang, *Tetrahedron Lett.*, **39**, 4199 (1998).
6. A.M. Daly, C.T. Dalton, M.F. Renehan and D.G. Gilheany, *Tetrahedron Lett.*, **40**, 3617 (1999).
7. M. Tokunaga, J.F. Larrow, F. Kakiuchi and E.N. Jacobsen, *Science*, **277**, 936 (1997).
8. J.P. Collman, V.J. Lee, C.J. Kellen-Yuen, X. Zhang, J.A. Ibers and J.I. Brauman, *J. Am. Chem. Soc.*, **117**, 692 (1995).
9. K.J. Ballus, A.K. Khanmamedova, K.M. Dixon and F. Bedioui, *Appl. Catal. A*, **143**, 159 (1996).
10. C. Heinrichs and W.F. Holderich, *Catal. Lett. Catal. Lett.*, **58**, 75 (1999).
11. G.J. Kim and J.H. Shin, *Tetrahedron Lett.*, **40**, 6827 (1999).
12. D.W. Park, S.D. Choi, S.J. Choi, C.Y. Lee and G.J. Kim, *Catal. Lett.*, **78**, 145 (2002).
13. C. Mossner and C. Bolm, in eds.: M. Beller and C. Bolm, *Transition Metals for Organic Synthesis*, Wiley-WCH Verlag, Weinheim, edn 2, pp. 389–402 (2004).
14. Z. Li, K.R. Conser and E.N. Jacobsen, *J. Am. Chem. Soc.*, **115**, 5326 (1993).
15. C.R. Jacob, S.P. Varkey and P. Ratnasamy, *Micropor. Mesopor. Mater.*, **22**, 465 (1998).
16. P. Klement, F. Stock, H. Elias, H. Paulus, P. Pelikán, M. Valko, M. Mazúr, *Polyhedron*, **18**, 3617 (1999).
17. Z. Li, Z. Zheng, B. Wan and H. Chen, *J. Mol. Catal. A*, **165**, 67 (2001).
18. Y.N. Belokon, J. Fuentes, M. North and J.W. Steed, *Tetrahedron*, **60**, 3191 (2004).
19. C. Bianchini and P. Barbaro, *Top. Catal.*, **19**, 17 (2002).
20. C.E. Song and S.G. Lee, *Chem. Rev.*, **102**, 3495 (2002).
21. A.R. Silva, M.M.A. Freitas, C. Freire, B. de Castro and J.L. Figueiredo, *Langmuir*, **18**, 8017 (2002).
22. P. Memorn and C. Hutchings, *J. Soc. Rev.*, **33**, 108 (2004).
23. C. Li, *Catal. Rev. Sci. Eng.*, **46**, 419 (2004).
24. V. Ayala, A. Corma, M. Iglesias and F. Sánchez, *J. Mol. Catal.*, **221**, 201 (2004).
25. A. Sakthivel, J. Zhao, G. Raudaschl-Sieber, A.S.T. Chiang and F.E. Kühn, *Appl. Catal. A*, **281**, 267 (2005).
26. H. Zhang, S. Xiang and C. Li, *Chem. Commun.*, 1209 (2005).
27. A. Sakthivel, J. Zhao and F.E. Kühn, *Catal. Lett.*, **102**, 115 (2005).
28. F.E. Murphy, L. Schmid, T. Buerger, M. Maciejewski, A. Baiker, D. Guenther and M. Schneider, *Chem. Mater.*, **13**, 1296 (2001).
29. P. Karandikar, K.C. Dhanya, S. Deshpande, A.J. Chanwadkar, S. Sivasanker and A. Agashe, *Catal. Commun.*, **5**, 69 (2004).
30. R.A. Sheldon and J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York (1981).
31. M. Yazdanbakhsh, M.M. Heravi, R. Takjoo and W. Frank, *Z. Anorg. Allg. Chem.*, **634**, 972 (2008).
32. F. Bedioui, *Coord. Chem. Rev.*, **144**, 39 (1995).