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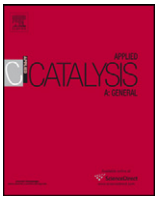

Copper on boehmite: A simple, selective, efficient and reusable heterogeneous catalyst for oxidation of alcohols with periodic acid in water at room temperature

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ABSTRACT

Oxidation of various aliphatic, aromatic, alicyclic, benzylic and allylic alcohols to corresponding carbonyl compounds is studied in water at room temperature over copper on boehmite [Cu/AlO(OH)] catalyst which is prepared from $CuCl_2 \cdot 2H_2O$, pluronic P123 and Al(O-*sec*-Bu)$_3$. The prepared catalyst was characterized by HR-TEM, SEM-EDX and IR spectroscopy. The reaction conditions for catalytic oxidation of alcohols are optimized with different mole ratio, solvents, and oxidants using 1-phenylethanol system as a model. The scope of the reaction is extended to various types of alcohols. Chemoselectivity, heterogeneity and reusability tests were performed. The use of water as a solvent at room temperature makes the reaction interesting from both an economic and environmental point of view.

1. Introduction

Selective oxidation of alcohols to carbonyl compounds is one of the most pivotal functional group transformations in organic synthesis [1–8], since the products are valuable both as intermediates as well as being high value components for the perfumery industry [1,9,10]. Aldehydes of low molecular weight are condensed in an aldol reaction to produce derivatives used in the plasticizer industry. Traditionally, oxidation of alcohols are performed with stoichiometric amounts of inorganic oxidants, notably chromium(VI) reagents [11]. These oxidants are not only relatively expensive, but they also generate copious amounts of heavy-metal waste and have toxic issues. Moreover, the reactions are often performed in environmentally undesirable solvents, typically chlorinated hydrocarbons. There are some milder oxidation reactions using Swern and Dess–Martin reagents [12,13]. Swern oxidation releases toxic volatile by-products such as dimethyl sulfide and carbon monoxide. Dess–Martin periodinane was prepared from 2-iodoxybenzoic acid which usually decomposes explosively. Although individually having some synthetic advantages, most methods suffer from one or more experimental drawbacks such as severe reaction conditions, complicated reaction procedures and need to use toxic solvents. To overcome this, various catalytic methods for the oxidation of alcohols have been developed recently [14]. Hence, the exploration of a mild but efficient oxidation method with easy handling and nontoxic green solvent is a challenging area of research in organic synthesis. Many examples of homogeneous systems make use of palladium [15], copper [7] or ruthenium compounds [16], typically in toluene as solvent. The use of an organic solvent, such as toluene, necessitates a tedious distillation and cumbersome recovery of the catalyst. Furthermore, the method is not suitable for products that have boiling points close to that of the organic solvent used.

Hypervalent iodine reagents have attracted increasing interest as oxidants in organic synthesis due to their mild, selective and environmentally benign oxidizing properties [17]. Periodic acid is used as oxidant in several mild and selective oxidation reactions. Chromium trioxide [18], pyridinium chlorochromate [19], fluorochromate [20], bis(trimethylsilyl)chromate [21], chromiumtris(acetylacetonate) [22], Fe(III)/2-picolinic acid [23] and KBr [24] have been used as catalysts for the oxidation of alcohols with periodic acid. But those reactions are carried out in chlorinated solvents or other organic solvents and sometimes at elevated temperatures. Hence, we herein report an effective procedure for the selective oxidation of alcohols to the corresponding carbonyl compounds catalyzed by Cu/AlO(OH) using H_5IO_6 as oxidant in water at room temperature. Preparation of catalyst is simple

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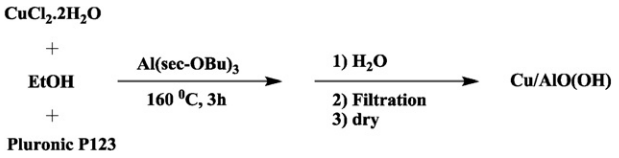


Scheme 1. Preparation of catalyst, Cu/AlO(OH).

and no toxic by-products are released in the present catalytic system.

2. Experimental

2.1. Materials

All the reagents used were of chemically pure and analar grade. Commercial grade solvents were distilled according to normal procedures and dried over molecular sieves before use. All other chemicals were purchased from Aldrich and were used without further purification.

2.2. Catalyst preparation

Catalyst was prepared by following literature procedure [25]. $CuCl_2{\cdot}2H_2O$ (400 mg, 2.3 mmol), pluronic P123 (4.0 g) [$EO_{20}PO_{70}EO_{20}$ (EO = ethylene oxide, PO = propylene oxide)], and absolute ethanol (10 mL) were added in 100 mL round bottomed flask equipped with a condenser. To get a solution, this mixture was stirred for 30 min at room temperature. Al(O-*sec*-Bu)$_3$ (9.1 g, 37 mmol) was added carefully. After being stirred at 160 °C for 3 h, 3 mL of water was added. The reaction mixture was stirred further for 30 min at 160 °C, cooled down and kept at room temperature for 3 h. The resulting bluish solid was filtered, washed with acetone, and dried at 120 °C for 2 h to give a bluish green powder (3 g, 3.2 wt.% of Cu) (Scheme 1). The copper content was estimated by SEM-EDX analysis.

2.3. Catalyst characterization

HR-TEM analysis was done in Hitachi instrument. SEM-EDX data were recorded in Hitachi SU6600 scanning electron microscope. The electronic spectra were recorded in PG Instrument T90+ spectrophotometer. The IR spectra were recorded in Perkin Elmer FT-IR spectrometer using KBr plates. Gas chromatographic analysis is done in Shimadzu-2010 gas chromatograph (GC).

2.4. Oxidation of alcohols

Catalyst (15.25 mg, 1 mol%) and H_5IO_6 (0.2279 g, 1 mmol/2 equiv.) were stirred with 10 mL of H_2O taken in the round bottomed flask. The substrate (0.5 mmol/1 equiv.) was added slowly to the stirring solution. Stirring was continued for required time at room temperature. After the requisite time, the catalyst was separated by centrifugation. The centrifugate was decanted slowly and the product was extracted with diethyl ether. The ether extract was evaporated. Then the product was dissolved in double distilled acetone and then analysed by GC. Authentic samples of both reactant and products were used to verify the retention times and to confirm the product formation. The ether extract was concentrated and chromatographed on a silica gel column with n-hexane:ethanol (4:1) as the eluting solvent to give carbonyl product. The used catalyst was washed with diethyl ether and then it was reused for the subsequent oxidation of alcohol for testing the catalyst reusability.

2.5. Product analysis

Gas chromatograph is equipped with 5% diphenyl and 95% dimethyl siloxane, Restek capillary column (60 m length, 0.32 mm dia) and a flame ionization detector (FID). The initial column temperature was increased from 60 to 150 °C at the rate of 10 °C/min and then to 220 °C at the rate of 40 °C/min. Nitrogen gas was used as a carrier gas. The temperatures of the injection port and FID were kept constant at 150 and 250 °C, respectively during product analysis.

3. Results and discussion

3.1. Catalyst preparation and characterization

$CuCl_2{\cdot}2H_2O$, pluronic P123 and absolute ethanol were stirred in 100 mL round bottomed flask equipped with a condenser for 30 min at room temperature. To the solution, Al(O-*sec*-Bu)$_3$ was added carefully. After being stirred at 160 °C for 3 h, water was added. The reaction mixture was stirred further for 30 min at 160 °C, cooled down and kept at room temperature for 3 h. The resulting bluish solid was filtered, washed with acetone, and dried at 120 °C for 2 h to give a bluish green powder (Scheme 1).

The SEM images of the catalyst suggest that the particle size of boehmite matrix is in the range of 20–30 μm above which Cu nanoparticles are adsorbed. This was further confirmed by HR-TEM analysis. The size of Cu nanoparticles was found to be 20–30 nm from HR-TEM analysis (Fig. 1). From the SEM-EDX result, Cu weight percentage is found to be 3.2%. This value matches with the already

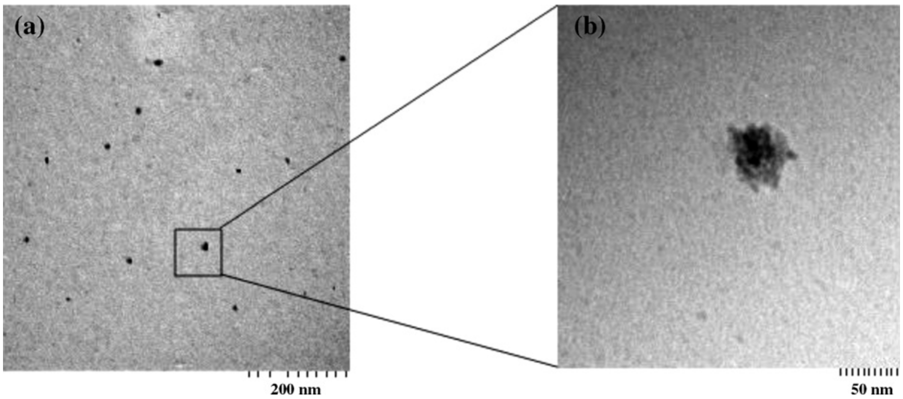


Fig. 1. HR-TEM Images: (a) low resolution (20 nm bar scale), (b) high resolution (5 nm bar scale).

Table 1
Effect of oxidant, catalyst amount and temperature on oxidation of 1-phenylethanol.

Entry	Substrate (equiv.)	Catalyst (mol%)	Oxidant (equiv.)	Time (h)	Temperature (°C)	Yield[a] (%)
1	1	2	0.5	15	27	33
2	1	4	2.0	15	27	83
3	1	4	2.0	15	60	11
4	1	4	4.0	5	27	71
5	1	1	2.0	5	27	96
6	1	0	2.0	5	27	12

[a] GC yield.

reported literature value [25]. In the IR spectrum, peak at 3400 cm^{-1} corresponds to OH stretching frequency. The peak at 1075 cm^{-1} has been assigned as due to Al=O stretching frequency. The other peaks at 1644 cm^{-1}, 1111 cm^{-1}, 624 cm^{-1} and 516 cm^{-1} correspond to Al–O stretching and bending frequencies [26].

3.2. Optimization of reaction conditions

In order to get effective results, the reaction variables such as solvent, oxidant, amount of oxidant and amount of catalyst were optimized. For this purpose, 1-phenylethanol was chosen as a model substrate. The completion of the reaction is monitored through GC.

The reaction was studied at different mole ratios of 1-phenylethanol, catalyst, and periodic acid (Table 1). In order to get good yield, the mole ratio of the oxidant is increased and the mole ratio of catalyst is decreased. This is because, as the mole ratio of the oxidant is increased the oxygen supply to the substrate is increased and hence, the reaction proceeds well with good yield. Similarly, as the mole ratio of the catalyst is decreased, the substrate may interact with the oxo species effectively as the distance between substrate and oxo species might be lower. This favors the oxidation process. A blank run i.e., the reaction carried out in the absence of the catalyst gives very little conversion (only 12%).

The experiment has been conducted at room temperature in different solvents (dichloromethane, acetonitrile, toluene or water) taking 1 equiv. of 1-phenylethanol, 1 mol% of the catalyst and 2 equiv. of periodic acid in a round bottom flask (Fig. 2). Since the solubility of the oxidant periodic acid is good in water the reaction proceeds well in water solvent when compared to the others. Also, the catalyst is more dispersed in water medium than any other solvents. It enhances the catalytic activity.

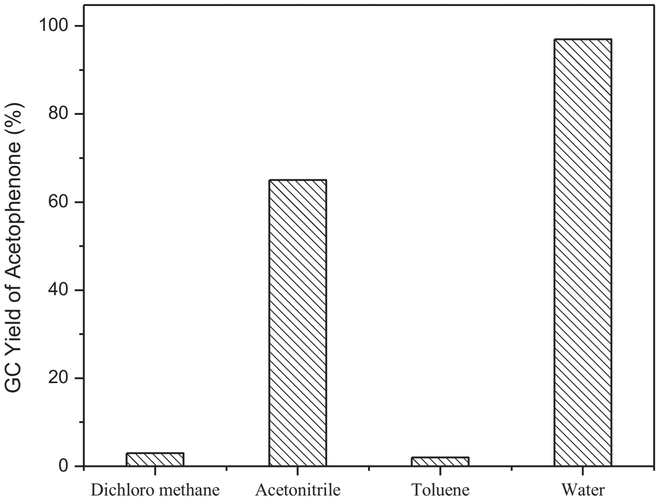


Fig. 2. Effect of solvent on oxidation of 1-phenylethanol.

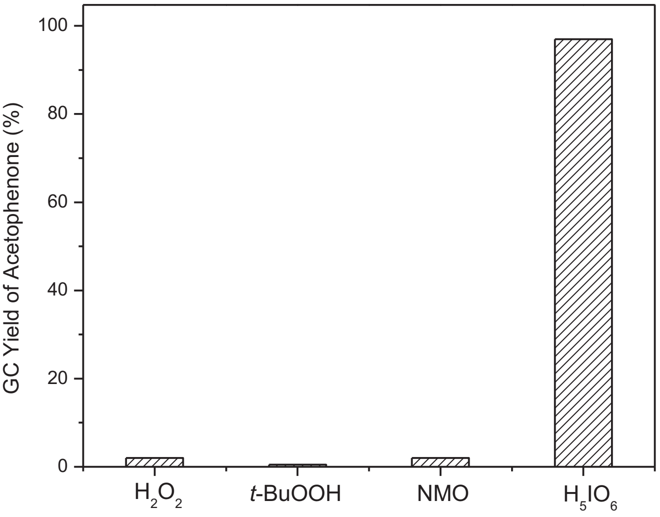


Fig. 3. Effect of oxidant on oxidation of 1-phenylethanol.

The experiment has been conducted at room temperature with different oxidants (2 equiv.) *viz.* hydrogen peroxide, *t*-butyl hydroperoxide, *N*-methylmorpholine-*N*-oxide (NMO) or periodic acid, taking 1 equiv. of 1-phenylethanol and 1 mol% of the catalyst in a round bottom flask with 10 mL of water (Fig. 3). The yield is tremendously increased after introducing 2 mmol of periodic acid as oxidant in shorter reaction time. From the optimization studies, it is evident that water is the best solvent and periodic acid is the best oxidant for the present catalytic system.

3.3. Extension of scope

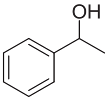
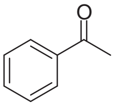
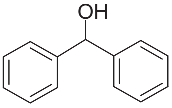
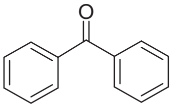
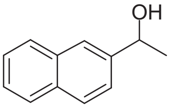
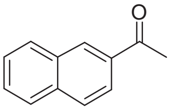
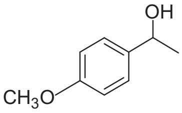
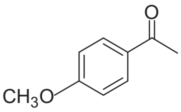
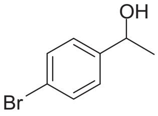
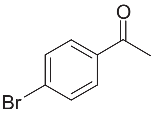
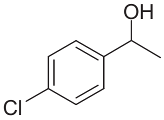
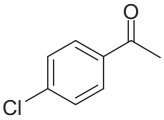
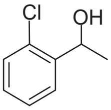
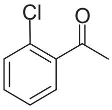
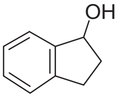
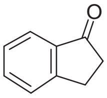
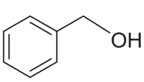
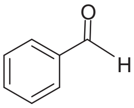
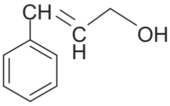
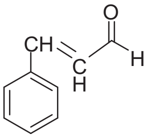
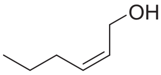
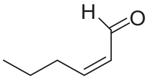
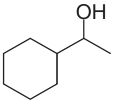
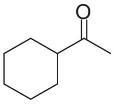
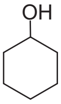
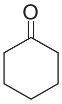
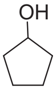
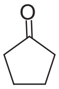
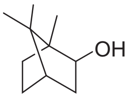
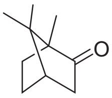
To establish the generality of the method, both primary and secondary allylic, benzylic and aliphatic alcohols were oxidized with periodic acid to give corresponding carbonyl compounds in good to excellent yields and results are shown in Table 2.

Oxidation of alcohols is a dehydrogenation process. The removal of H from the CH or CH_2 group is difficult. When an electron with drawing group is attached with CH or CH_2 group, CH or CH_2 proton(s) become(s) more acidic, highly reactive and hence easily removed. Active aryl secondary alcohols such as 1-phenylethanol, diphenylcarbinol and 1-indanol can be smoothly oxidized to acetophenone, benzophenone and 1-indanone with excellent yields, respectively (Table 2, entry 1, 2 and 8). Considering the mesomeric effect at the 1-phenylethanol system, electron donating substituents such as methoxy, phenyl, bromo and chloro groups decrease the yield considerably (Table 2, entry 3–6). Presence of chloro group at the second position in 1-(2-chlorophenyl)-ethanol decreases the yield of the corresponding carbonyl compound due to steric hindrance (Table 2, entry 7).

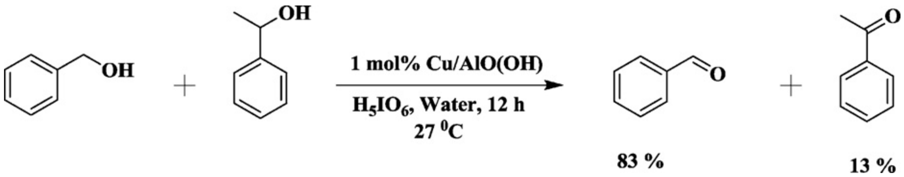
Oxidation of α-methyl-2-naphthalene methanol (Table 2, entry 3) yielded the aldehyde without the oxidation of naphthalene ring unlike the CrO_3/H_5IO_6 oxidation [27]. In the conversion of 1-indanol to 1-indanone (Table 2, entry 8), present catalytic system (with the yield of 95% after 3 h) is better compared to KBr catalyzed oxidation [24] as well as Ru-catalyzed oxidation [28] (83% after 5 h) with the same oxidant. It is worthwhile to mention that oxidation of benzyl alcohol proceeds well with this system to give 93% yield of benzaldehyde without any appreciable over oxidation to the corresponding carboxylic acid (Table 2, entry 9).

Oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds is an interesting process in the view of chemoselectivity. It was found that cinnamaldehyde was obtained from cinnamyl alcohol in 41% yield after 7 h of stirring (Table 2, entry 10)

Table 2
Oxidation of alcohols[a].

Entry	Substrate	Product	Time (h)	Conversion[b] (%)	Selectivity[b] (%)	Yield[b] (%)
1			5	99	97	97
2			3	97	100	97 (91)[c]
3			3	95	99	94 (87)[c]
4			5	98	94	92 (87)[c]
5			10	99	99	98 (94)[c]
6			8	90	100	90 (82)[c]
7			13	78	100	78
8			3	99	96	95 (93)[c]
9			7	99	94	93
10			7	56	73	41
11			24	34	100	34
12			24	78	95	74
13			10	53	81	43
14			24	35	100	35
15			24	16.1	100	16

[a] Reaction conditions: Substrate (1 equiv.), Cu/AlO(OH) (1 mol%), H_5IO_6 (2 equiv.), water (10 mL), 27 °C.
[b] Determined by GC analysis.
[c] Isolated yield is given in parenthesis.



Scheme 2. Chemoselectivity of catalyst, Cu/AlO(OH).

whereas $NaIO_4$/2,2,6,6-tetramethylpiperidine-1-oxy/NaBr system gives only 18% of aldehyde from the same substrate [29]. In the same way oxidation of cis-hexen-1-ol gives the corresponding α,β-unsaturated carbonyl compound, the yield is 34% (100% selectivity) after 24 h of stirring (Table 2, entry 11). Solubility of few solid substrates particularly diphenylcarbinol, α-methyl-2-naphthalene methanol and 1-indanol is less in water but reaction proceeds well without causing any trouble which is difficult in other systems [30,31].

1-Cyclohexylethanol is converted into its corresponding ketone in 74% yield after stirring for 24 h (Table 2, entry 12). The only shortcoming of this method is less sensitivity towards aliphatic alcohols. Cyclohexanol and cyclopentanol are converted to cyclohexanone (43% yield) and cyclopentanone (35% yield) after 10 h and 24 h respectively (Table 2, entry 13 and 14). In the case of aliphatic and alicyclic alcohols, slower oxidation required longer reaction time. The oxidation of DL-isoborneol cannot be completed within 24 h, due to the steric hindrance from the bridge head (Table 2, entry 15).

3.4. Chemoselectivity

To study the chemoselectivity, a mixture of primary and secondary alcohols was subjected to oxidation in presence of 1 mol% of catalyst. When benzyl alcohol and 1-phenylethanol were allowed to react, the former oxidized to benzaldehyde in 83% yield and the latter gave acetophenone in 13% yield (Scheme 2). The selective oxidation of benzyl alcohol in presence of 1-phenylethanol may be due to the fact that α-CH unit is more acidic than that of 1-phenylethanol [32]. This study clearly reveals that this method can be applied for the chemoselective oxidation of primary alcohols in the presence of secondary hydroxy groups.

3.5. Heterogeneous nature of the catalyst

In order to prove the heterogeneous nature of the catalyst and the absence of Cu leaching, a heterogeneity test was performed, in which the catalyst was separated from the reaction mixture at approximately 61% conversion of the starting material through centrifugation. The reaction progress in the filtrate is monitored (Fig. 4). No further oxidation occurs even at extended times, indicating that no active species (copper) leach from the support during reaction.

3.6. Reusability

The recycling of the catalyst is very important for industrial application. After centrifugation and washing with diethyl ether, we could reuse Cu/AlO(OH) catalyst with 3.2 wt% Cu for the oxidation of α-methyl-2-naphthalene methanol and results are shown in Fig. 5. The oxidation reaction was carried out 4 times under identical reaction conditions with the recycling of Cu/AlO(OH) catalyst. The yield of product was 88% at the 1st run. No significant decrease was observed in the 2nd run as the yield of product was 87%. There is a slight decrease in the yield of product during 3rd (83%) and 4th (82%) run. The yield, however was still good and indicating an excellent reusability of the catalyst.

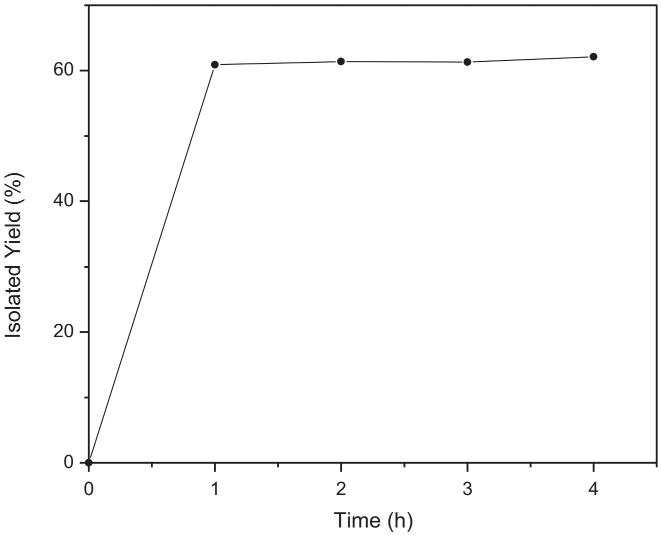


Fig. 4. Heterogeneity test for oxidation of α-methyl-2-naphthalene methanol. [Reaction conditions: α-methyl-2-naphthalene methanol (86.11 mg, 0.5 mmol/1 equiv.), Cu/AlO(OH) (15.25 mg, 1 mol%), H_5IO_6 (0.2279 g, 1 mmol/2 equiv.), water (10 mL), 27 °C].

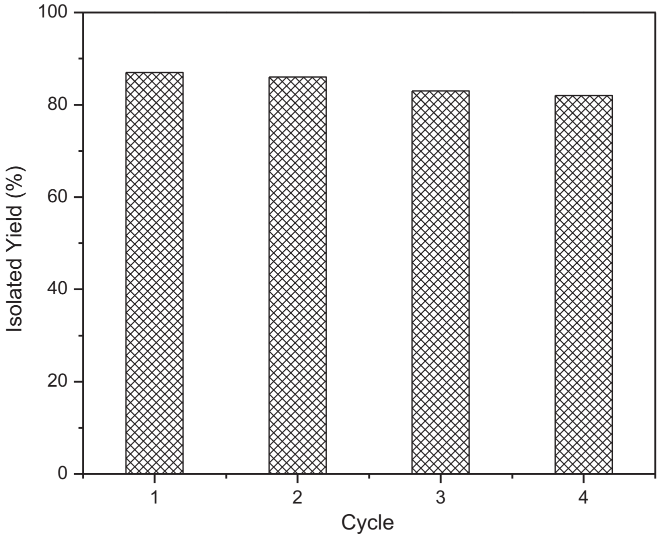


Fig. 5. Reusability of Cu/AlO(OH) for oxidation of α-methyl-2-naphthalene methanol.

4. Expected mechanism

Based on the observation, typical mechanism proposed for Cu/AlO(OH) catalysed oxidation of alcohols with periodic acid is given in Fig. 6. In the first step the oxidant supplies oxygen to Cu present in catalyst to form an oxo species. In the second step the oxo species carry out the conversion of alcohols to the corresponding carbonyl compounds and the catalyst is regenerated. The result of chemoselectivity experiment is also in line with the proposed

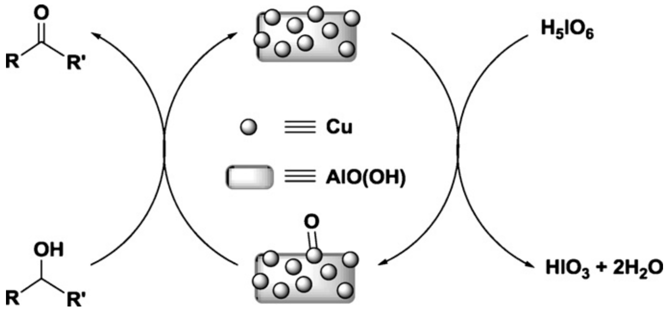


Fig. 6. Expected mechanism for the Cu/AlO(OH)-H_5IO_6 catalytic system.

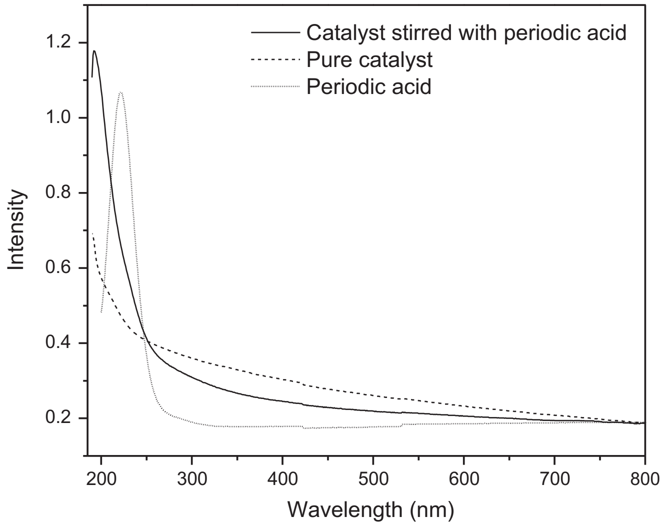


Fig. 7. UV–vis spectra of catalyst before and after adding periodic acid.

mechanism. The second step of the mechanism includes removal of α-hydrogen which is difficult in the case of 1-phenylethanol because of lower acidity of α-CH unit. Hence, benzyl alcohol is chemoselectively oxidized in presence of 1-phenylethanol.

The electronic spectra were analysed after sonicating 0.2 g of catalyst per liter of water for 30 min (Fig. 7). The pure catalyst [Cu/AlO(OH)] does not give any absorption peak in UV–vis region (190–800 nm). A band at 222 nm was observed for periodic acid. But the electronic spectrum of catalyst after being stirred with periodic acid shows an absorption maximum at 192 nm. This new absorption band may be due to the formation of Cu-oxo species.

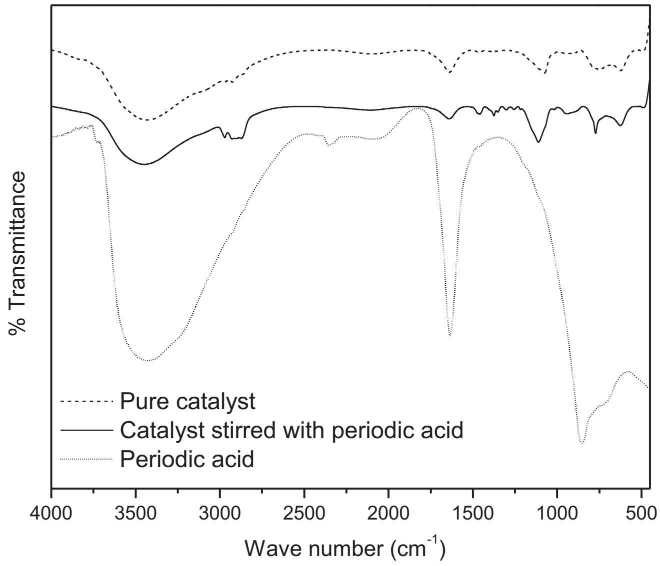


Fig. 8. FT-IR spectra of catalyst before and after adding periodic acid.

The FT-IR spectra of pure catalyst [Cu/AlO(OH)], periodic acid and the catalyst after stirring with periodic acid (for 5 h) were recorded (Fig. 8). In the spectrum of pure catalyst, there is no sharp peak around 750 cm^{-1}. But the catalyst exhibits a weak band in this region which may be due to the presence of trace amount of CuO and Cu_2O. Periodic acid shows a strong band at 854 cm^{-1} due to I=O. Whereas in the spectrum of catalyst after stirring with periodic acid, there is a sharp peak at 757 cm^{-1} which may be due to the formation of Cu-oxo species. Similar spectral changes (UV–vis and FT-IR) have been observed during the conversion of Ru(II) to Ru(IV)-oxo species [32]. This suggests the formation of oxo species and also supports the proposed mechanism.

5. Conclusion

In conclusion, Cu/AlO(OH) was found to be a simple, selective, air stable, efficient and reusable heterogeneous catalyst for the oxidation of alcohols. Hence a new catalytic system which is mild, green and effective for oxidation of variety of alcohols into carbonyl compounds by using periodic acid as oxidant and Cu/AlO(OH) as catalyst in water at room temperature, has been developed. This procedure is environmentally benign, general, efficient, high yielding, safe and operationally simple.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.11.012.

References

[1] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
[2] M. Beller, C. Bolm, Transition Metals for Organic Synthesis, Second Edition, Wiley-VCH, Weinheim, 2004.
[3] G. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636–1639.
[4] M. Vazylyev, D. Sloboda-Rozner, A. Haimov, G. Maayan, R. Neumann, Top. Catal. 34 (2005) 93–99.
[5] M. Pagliaro, S. Campestrini, R. Ciriminna, Chem. Soc. Rev. 34 (2005) 837–845.
[6] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 26 (2004) 10657–10666.
[7] I.E. Marko, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Science 274 (1996) 2044–2046.
[8] M.J. Schultz, R.S. Adler, W. Zierkiewicz, T. Privalov, M.S. Sigman, J. Am. Chem. Soc. 127 (2005) 8499–8507.
[9] U.R. Pillai, E. Sahle-Demessie, Appl. Catal. A: Gen. 245 (2003) 103–109.
[10] M. Hudlicky, Oxidations in Organic Chemistry, ACS, Washington, DC, 1990.
[11] G. Cainelli, G. Cardillo, Chromium Oxidants in Organic Chemistry, Springer, Berlin, 1984.
[12] K. Omura, D. Swern, Tetrahedron 34 (1978) 1651–1660.
[13] D.B. Dess, J.C. Martin, J. Org. Chem. 48 (1983) 4155–4156.
[14] S.V. Ley, A. Madin, in: B.M. Trost, I. Flemming (Eds.), Comprehensive Organic Synthesis, vol.7, Pergamon Press, Oxford, 1991, p. 251.
[15] T. Nishimura, T. Onoue, K. Ohe, S. Uemura, Tetrahedron Lett. 39 (1998) 6011–6014.
[16] A. Dijkman, I.W.C.E. Arends, R.A. Sheldon, Chem. Commun. (1999) 1591–1592.
[17] A. Varvogils, Hypervalent Iodine In Organic Synthesis, Academic Press, San Diego, 1997.
[18] S. Zhang, L. Xu, M.L. Trudell, Synthesis (2005) 1757–1760.
[19] M. Hunsen, Tetrahedron Lett. 46 (2005) 651–653.
[20] M. Hunsen, J. Fluorine Chem. 126 (2005) 1356–1360.

[21] K. Asadolah, M.M. Heravi, R. Hekmatshoar, S. Majedi, Molecules 12 (2007) 958–964.

[22] L. Xu, M.L. Trudell, Tetrahedron Lett. 44 (2003) 2553–2555.

[23] S.S. Kim, I. Trushkov, S.K. Sar, Bull. Korean Chem. Soc. 23 (2002) 1331–1332.

[24] M.A. Zolfigol, F. Shirini, G. Chehardoli, E. Kolvari, J. Mol. Catal. A: Chem. 265 (2007) 272–275.

[25] M. Serk Kwon, Y. Kim, J. Sung Lee, J. Park, Org. Lett. 10 (2008) 497–500.

[26] S. Mathew, C.S. Kumara, N. Nagaraju, J. Mol. Catal. A: Chem. 255 (2006) 243–248.

[27] M. Zhao, J. Li, Z. Song, R. Desmond, D.M. Tschaen, E.J.J. Grabowski, P.J. Reider, Tetrahedron Lett. 39 (1998) 5323–5326.

[28] S. Ganesamoorthy, K. Shanmugasundaram, R. Karvembu, Catal. Commun. 10 (2009) 1835–1838.

[29] M. Lei, R.-J. Hu, Y.-G. Wang, Tetrahedron 62 (2006) 8928–8932.

[30] C.-J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68–82.

[31] P. Gogoi, D. Konwar, Org. Biomol. Chem. 3 (2005) 3473–3475.

[32] D. Chatterjee, A. Mitra, S. Mukherjee, J. Mol. Catal. A: Chem. 165 (2001) 295–298.