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Solvent free selective oxidation of alcohols catalyzed by a trinuclear complex with a dicopper(II)–monozinc(II) centre using hydrogen peroxide as an oxidant†

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The oxidation of alcohols to carbonyl compounds was investigated by an efficient catalytic system comprising of a new heterotrinuclear complex containing a dicopper(II)–monozinc(II) centre, $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$ with hydrogen peroxide under solvent free conditions. Primary and secondary alcohols were oxidized to the corresponding aldehydes and ketones in good to excellent yield. The newly developed catalyst system can be reused in four consecutive runs without any significant loss of activity.

Introduction

The selective oxidation of alcohols is one of the most widely employed transformations in organic synthesis.[1] Although numerous protocols are available, many employ stoichiometric or superstoichiometric heavy metal compounds like CrO_3, $KMnO_4$, MnO_2, SeO_2 *etc.*[2] Safety hazards associated with these oxidants and their toxic by-products and the difficulty to work up the reaction mixture are the main problems of such processes. One way to alleviate this problem is to rationally design catalytic systems that employ transition metals that readily activate oxidants like oxygen or hydrogen peroxide.[3,4] Consequently, a number of catalytic methods using complexes containing transition metals, such as Pd,[5] Ru,[6] Rh,[7] Mo,[8] Cu,[9] Co,[10] V[11] and clean oxidants such as dioxygen or hydrogen peroxide have been developed. From an economical and environmental view point, catalytic oxidation processes employing H_2O_2 are particularly attractive.

Among the above mentioned metal salts, Cu is more relevant, as it is biomimetic functional model of the multinuclear copper enzymes like particulate methane monooxygenase, laccase, ascorbate oxidase, human ceruloplasmin, fungal laccase, FET 3 and phenoxazinase.[12,13] As copper salt alone is an inefficient catalyst, a variety of ligands are used with copper salts to increase the catalytic activity. Unfortunately, most of these copper salt complexes need an external base for efficient oxidation.[9]

While there has been no lack of pioneering work on alcohol oxidation with aqueous hydrogen peroxide promoted by a homogeneous catalyst, the heterogeneous switching of catalytic oxidation to meet green chemical requirements still remains major challenge. Heterogeneous catalytic systems for the oxidation of alcohols with hydrogen peroxide would realize environmentally benign, secure processes as well as facilitated methods for product purification and catalyst recycling.[14] Inspired by natural metal containing enzymes, we are interested in studying the catalytic activity of the metal organic framework (MOFs) whose catalytic activity using O_2 or H_2O_2 as a terminal oxidant is hardly explored. One advantage of MOFs is that they do not require the addition of an external base to form the metal complexes to act as catalyst which have the potential to function as heterogeneous catalyst. Moreover, the use of heterogeneous catalyst in the liquid phase offers several advantages over homogeneous ones such as recovery and recycling, atom utility and enhanced stability. This is a clean technology process where compounds are formed free from contaminated by-products. It is quite surprising that only a few examples using cheap and green copper catalyst and hydrogen peroxide[9] are known so far. To the best of our knowledge, although reports are available on the use of MOFs as sole catalyst/heterogeneous catalysts in aerobic oxidation, no reports is available on their use as catalyst using H_2O_2 as terminal oxidant.

In the present work, we report the oxidation of benzylic alcohols to the corresponding carbonyl compounds in good yields using a new heterometallic trinuclear complex with di-Cu(II) and mono Zn(II) centre (MOF)[15] $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$ (Fig. 1) derived from polyfunctional disalicylaldehyde succinoyldihydrazone (H_4slsch)[16] (Fig. 2) as a

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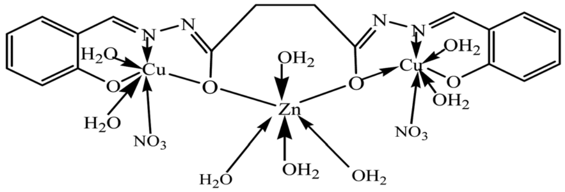


Fig. 1 Structure of the catalyst $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$.

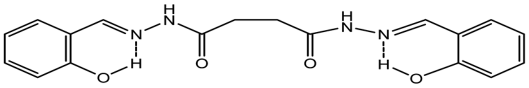
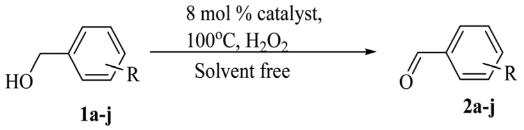


Fig. 2 Disalicylaldehyde succinoyldihydrazone (H_4slsch).



Scheme 1 Oxidation of alcohol using catalyst.

catalyst with hydrogen peroxide under solvent free condition (Scheme 1). 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.

Results and discussions

The details of catalyst preparation and characterization have been reported by us in our earlier publication.[15]

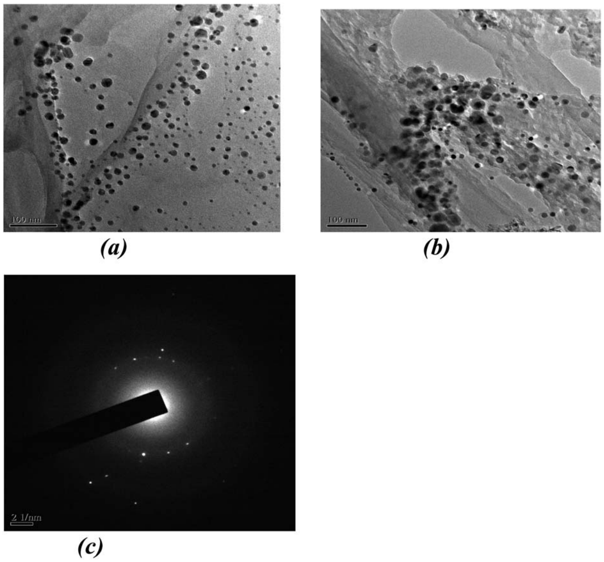

(a)
(b)
(c)

Fig. 3 TEM images of $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$ (a) before reaction; (b) after fourth run; (c) SAED of $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$.

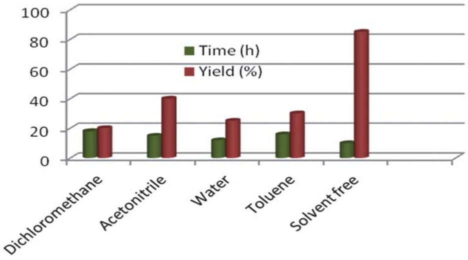


Fig. 4 Optimization of solvent effect on the model reaction.

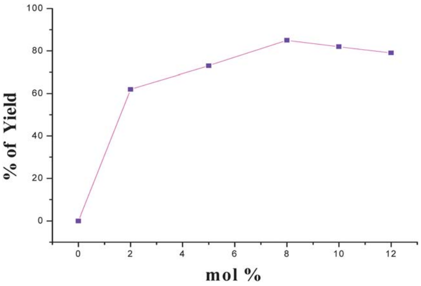
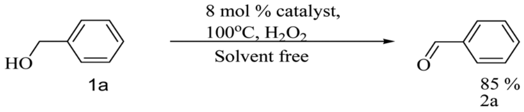


Fig. 5 Effect of catalyst loading on the model reaction.

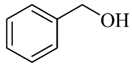
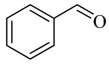
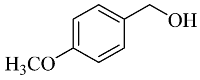
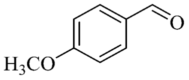
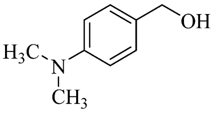
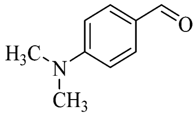
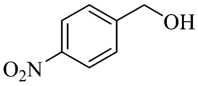
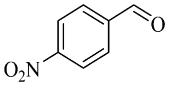
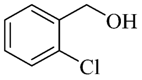
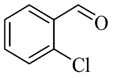
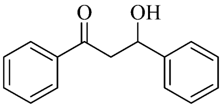
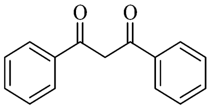
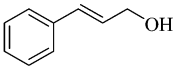
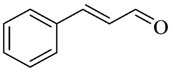
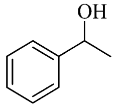
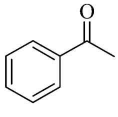
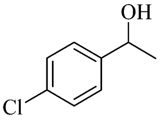
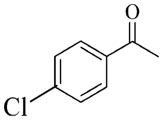
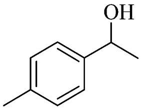
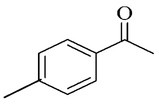
In order to know the nature of the particles TEM images of the catalyst was recorded which shows that the particles are spherical in shape with size in the range (12 ± 10) nm (Fig. 3a). The SAED shows the electron diffraction pattern of the selected area of nanoparticles. The SAED (Fig. 3c) shows moderately strong diffraction spots which confirm the formation of moderately single crystalline cube of the trimetallic complex.[17,18] TEM image of the catalyst was also recorded after four consecutive runs. It shows that the morphology of the catalyst does not change after the reaction which helps in the reusability of the catalyst for several runs (Fig. 3b).

Initial reaction to optimize the reaction conditions for oxidation of alcohols was carried out on benzyl alcohol. The reaction of **1a** was initially carried out using 5 mol% of catalyst, 30% H_2O_2 as oxidant in dichloromethane, afforded the product **2a** in 20% yield, characterized from spectral data as benzaldehyde (Fig. 4). The reaction was also performed using other solvents (acetonitrile, water and toluene), poor yields of the product **2a** was obtained (Fig. 4). Interestingly, it was found under solvent free condition, the catalyst converted benzyl alcohol to benzaldehyde in 85% yield at 100 °C (Fig. 4). On increasing the temperature to 120 °C the yield of **2a** decreased. Effect of other reaction parameters such as catalyst loading and reaction time was examined under solvent free condition. Best result was obtained using 8 mol% of catalyst (Fig. 5). On lowering the catalyst loading to 2 and 5 mol%, low yields of the product **2a** were obtained. On increasing the catalyst loading to



Scheme 2 Oxidation of benzyl alcohol to benzaldehyde.

Table 1 Hydrogen peroxide mediated oxidation of alcohols to aldehydes and ketones[a]

Entry	Substrate	Product	Time (h)	Yield[b] (%)
1	 1a	 2a	10	85
2	 1b	 2b	11	87
3	 1c	 2c	11	88
4	 1d	 2d	9	82
5	 1e	 2e	10	78
6	 1f	 2f	12	80
7	 1g	 2g	9	82
8	 1h	 2h	12	80
9	 1i	 2i	14	82
10	 1j	 2j	12	78

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

10 and 12 mol%, the reaction still proceeded smoothly accompanied by a drop in the isolated yield with longer reaction times. No conversion of benzyl alcohol to benzaldehyde was observed in the absence of the catalyst. Hence, the catalyst played an active role in the oxidation of alcohols.

The progress of formation of benzaldehyde from benzyl alcohol as a function of time using catalyst was studied (Fig. S2†). It was observed that the conversion increased initially with the progress of the reaction time, reached a maximum and then remained unchanged. A good isolated yield for the

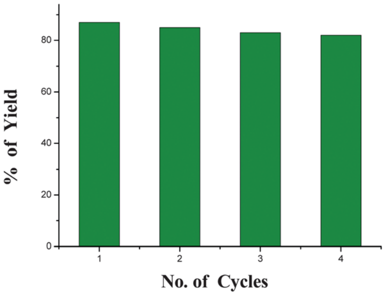


Fig. 6 Reusability chart of catalyst.

formation of benzaldehyde was observed at the optimum reaction time of 10 h (85%). Thus, the combination of catalyst (8 mol%), 30% H_2O_2 (10 mmol) at 100 °C under solvent free condition was found to be the most appropriate condition for the oxidation of alcohols (Scheme 2).

Encouraged by these results, the scope of reaction was extended to a variety of alcohols including primary and secondary aromatic alcohols using the above optimized reaction conditions, the results are summarized in Table 1. It was found that the alcohols were converted to the corresponding carbonyl compounds in good yield and excellent selectivity. Benzyl alcohols with substituents of varying electronic properties were all smoothly converted to the corresponding aldehydes (entries 2–5) in excellent yields. Electron donating substituents on benzyl alcohol gave slightly higher yields (entries 2 and 3). On the other hand electron withdrawing substituent on benzyl alcohol gave slightly lower yields (entries 4 and 5). The over oxidation to acid was not observed at all under the present reaction conditions with any of the alcohols. The conversion also proceeded smoothly even with cinnamyl alcohol without affecting the carbon–carbon double bond (entry 7). It was found that benzil was obtained in good yield from benzoin (entry 6). The secondary alcohols, 1-phenyl ethanol and substituted 1-phenyl ethanol were equally reactive affording the corresponding ketones in about 78–82% yield (entries 8–10).

Recovery and reusability of the catalyst

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 benzaldehyde; the data obtained are shown in (Fig. 6). No significant loss of efficiency was observed after four runs. This was also confirmed from the TEM image of the catalyst recorded after the fourth run (Fig. 3b).

Experimental section

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.[19] The study of morphology was performed by JEOL-JSM 6360CX with tungsten filament using a Si(Li) detector with a resolution 3 nm. Transmission electron microscopy images were measured on a JEOL-JEM-2100CX electron microscope operated at 200 kV without the addition of a contrast agent since the presence of the metal ion provided enough contrast. Melting points were recorded in open capillaries and are uncorrected. The FT-IR spectrum of the samples was recorded on a Perkin-Elmer FT-IR system, Spectrum BX, infrared spectrophotometer using KBr pellets. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance-400 spectrometer and Jeol-300 spectrometer.

Typical procedure for one pot conversion of alcohols to aldehydes and ketones catalyzed by $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$

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 (10 mmol) 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 ethyl acetate (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–j**.

Spectral data of compounds 2a and 2h

Benzaldehyde (2a). Ir (KBr): 2852, 2743, 1687 cm^{-1}. ^1H ($CDCl_3$, 300 MHz): $\delta = 10.00$ (s, 1H), 8.17 (d, $J = 7.5$ Hz, 1H), 7.88 (d, $J = 6.9$ Hz, 2H), 7.64–7.43 (m, 2H).

Acetophenone (2h). Ir (KBr): 2928, 1686 cm^{-1}. ^1H ($CDCl_3$, 300 MHz): $\delta = 7.95$ (d, $J = 7.2$ Hz, 2H), 7.56–7.41 (m, 3H), 2.58 (s, 3H). ^{13}C ($CDCl_3$, 75 MHz): $\delta = 197.9$, 136.9, 133.0, 128.2, 26.5.

Conclusions

In conclusion, we have developed a simple, efficient and environmentally benign process for the oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds using $[ZnCu_2(slsch)(NO_3)_2(H_2O)_8]\cdot 2H_2O$ as a heterogeneous catalyst under solvent free condition in good yields. The straightforward recovery of catalyst, reusability until the fourth run without substantial loss in activity and selectivity and use of hydrogen peroxide as oxidant are some features of the present work.

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