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Oxygen Bridged Bimetallic $CuMoO_4$ Nanocatalyst for Benzylic Alcohol Oxidation; Mechanism and DFT Study

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Abstract: Though concept of oxygen bridged bimetallic catalyst for organic reaction is not well understood. Herein, we have tried to explain the concept by experimental as well as its support by full DFT study. We report here a competent protocol for dehydrogenative oxidation of benzylic alcohol using an oxygen bridged bimetallic $CuMoO_4$ nano catalyst. Careful demonstration reveals that oxidation is not effective either with mono-metallic Cu (II) or Mo(VI); instead combination of both the metals through the oxygen bridge [Cu–O–Mo] unexpectedly and interestingly catalyzed the reaction efficiently. The new concept is strongly supported by computational DFT study. DFT study reveals dehydrogenative oxidation is preferred at copper centre over molybdenum and aromatic benzyl alcohols are greatly stabilised. Interaction barrier energy of monometallic CuO and MoO_3 catalyst is much higher than bimetallic $CuMoO_4$. Hydrogen transfer has larger barrier heights for CuO (31.5 kcal/mol) and MoO_3 (40.3 kcal/mol) than bimetallic $CuMoO_4$.

Oxidations of alcohols resulting carbonyl compounds are flexible organic sythons that can be transformed to various important compounds useful in biological and pharmaceutical industry.[1] However, fine chemical industry require a clean technology for alcohol oxidation without oxidizing other atoms and controlling over oxidations to acid; in presence of suitable metal source and oxygen source. Often the oxidation requires activators such as peroxide, nitroxyl radical and disposal of waste become tedious task in scale-up technology.[2] Moreover, atom economy process with low *E*-factor (waste/product), high turn over number (TON) and turn over frequency (TOF) are another important parameter for scale-up technology.[3] Traditional alcohol oxidation uses stoichiometric metal oxidants and peroxide at high temperature.[4] Subsequently, catalytic homogeneous[4] and heterogeneous[5,6,7,8] methods were employed with use of molecular oxygen (O_2) and air as the oxygen source using different transition metal salts (Pd, Ru, Mn, V, Co, Mo, Cu etc.). Among the transition metals used for alcohol oxidation, Pd- and Cu-catalyst takes the advantage over other catalyst for selective alcohol oxidation. Palladium metals has been successfully implemented for alcohol oxidation by Larock,[8a] Uemura,[8b] Sigmon,[8c] Stoltz,[8d] Stahl,[8e] Sun,[8f] Sheldon,[8g] Beller,[8h] Gao,[8i] et al. in presence of molecular oxygen. Sensitiveness to moisture and cost of palladium has compelled the chemist to choose and search alternative copper catalyst. Copper is one of the cheaper, eco-friendly and most abundant metal in earth crust.[9] Copper based catalyst systems employing TEMPO or a dialkylazodicarboxylate as redox-active cocatalysts have emerged as one of the most effective catalyst for alcohol oxidation in presence of molecular oxygen.[10–15] CuCl-TEMPO,[10a] CuCl-Phenanthrene/DBAD).[10b–d] Cu-bipyridine/ of KO^{t}Bu,[11a–b] CuI/TEMPO[11c–g] has been used successfully by Semmelhack, Markó, Sheldon and Stahl et al for selective oxidation of benzyllic and allylic alcohols using air as terminal oxidant.

Both Pd- and Cu-based catalyst has been implemented successfully by the use of amine based ligand[12] (1,-10 phenanthrene, DEAD/DIAD/DBAD) in presence of activator nitroxyl radical (TEMPO, NaOCl, NMI, ABNO), organic peroxide and molecular oxygen.[13] In addition to copper based catalyst;[14] molybdenum catalyst also been used for alcohol oxidation by several group. Trost et al used $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ catalyst with 30% H_2O_2[14] whereas Muratz et al used catalytic Mo/ Adogen-464 with sodium percarbonate.[15] Supported Mo-polyaniline catalyst has been used for alcohol oxidation by Punniyamurthy et al.[4] However, most of the copper catalyst system is not efficient for oxidation of secondary alcohol to ketones.

To balance the limitation of ligand and activator based Pd- and Cu- catalyst for alcohol oxidation; we were interested to employ [Cu–O–Mo] oxygen bridged bimetallic nanocatalyst $CuMoO_4$ for alcohol oxidation. It is well established that nano-catalyst works in absence of ligand with unusual selectivity and reactivity in well disperse solvent due to high surface area.[16–17] Furthermore the nano-catalyst is easily recyclable and environmentally benign process. Though concept of oxygen bridged bimetallic nano-catalyst [M^1–O–M^2] is not understood so much, but a diminutive development has been done so far by our group.[18]

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We have demonstrated the concept through a pictorial presentation (Figure 1) and it was well supported by DFT study.[19,20] An preliminary electron transfer concept could be understood from bimetallic hydroxo-bridged mixed-valent Cu(II)–Cu(III) and symmetric Cu(III)–Cu(III) (Figure 2). They undergo two reversible 1-electron oxidations, which explains well the oxidative capability of the oxo-bridged bimetallic catalyst (Figure 2).[21]

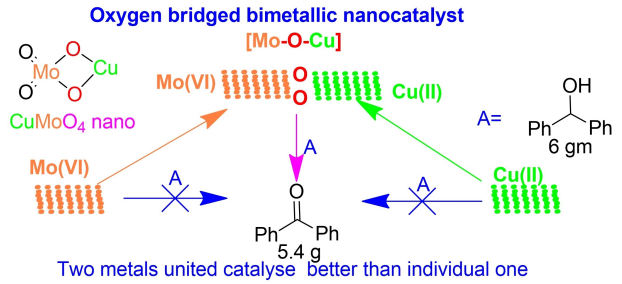


Figure 1. New Concept and Designing [Cu–O–Mo] oxo-bridged bimetallic catalyst.

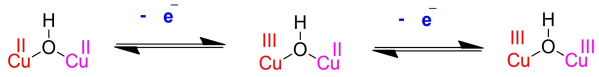
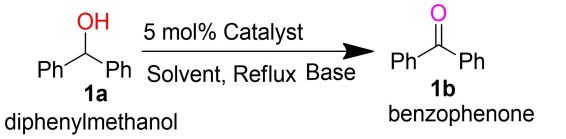


Figure 2. Hydroxo-bridged dicopper(II,III) and -(III,III) complexes in oxidation catalysis.[21]

Table 1. Oxidation of diphenyl methanol with $CuMoO_4$ nano catalyst.



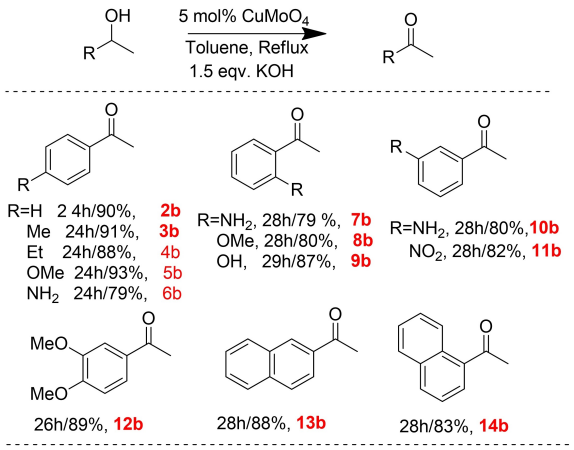
Entry	Catalyst	Base	Solvent	Yield [%][a,b]
1	$CuMoO_4$ nano	NaOH	Toluene	30
2	$CuMoO_4$ nano	KOH	Toluene	95
3	$CuMoO_4$ nano	KOH	Toluene	70[c]
4	$CuMoO_4$ nano	KOH	Toluene	45[d]
5	$CuMoO_4$ nano	KOH	Toluene	25[e]
6	$CuMoO_4$ nano	KOH	Toluene	15[f]
5	$CuMoO_4$ nano	K-O^{t}Bu	Toluene	60
7	$CuMoO_4$ nano	Cs_2CO_3	Toluene	30
8	$CuMoO_4$ nano	K_2CO_3	Toluene	20
9	$CuMoO_4$ nano	Na_2CO_3	Toluene	10
10	$CuMoO_4$ nano	K_3PO_4	Toluene	0
11	$CuMoO_4$ nano	Pyridine	Toluene	0
12	$CuMoO_4$ nano	NEt_3	Toluene	0
13	$CuMoO_4$ nano	KOH	CH_3CN	80
14	$CuMoO_4$ nano	KOH	DMF	55
15	$CuMoO_4$ nano	KOH	t-BuOH	60
16	$CuMoO_4$ nano	KOH	1,4-dioxane	45
17	–	KOH	Toluene	0[g]
18	$CuMoO_4$ nano	–	Toluene	0[h]
19	MoO_3	KOH	Toluene	<5
20	CuO	KOH	Toluene	<5
21	$CuMoO_4$ nano	KOH/O_2	Toluene	90[i]
22	$CuMoO_4$ nano	KOH	Toluene	90[j]
23	–	KOH/air	Toluene	0[k]

[a] Alcohol (2 mmol), $CuMoO_4$ nano, catalyst (5 mol%, 11 mg), base (1.5 equ.) were stirred in a 25 ml flask in 2 ml solvent under reflux condition for 24 h, [b] Isolated yield, [c] KOH (1 eq.), [d] KOH (0.75 eq.), [e] KOH (0.5 eq.), [f] KOH (0.2 eq.), [g] No catalyst, [h] No KOH, [i] O_2 ballon used, [j] 4 Å molecular sieve (250 mg) is used. [k] No catalyst and air.

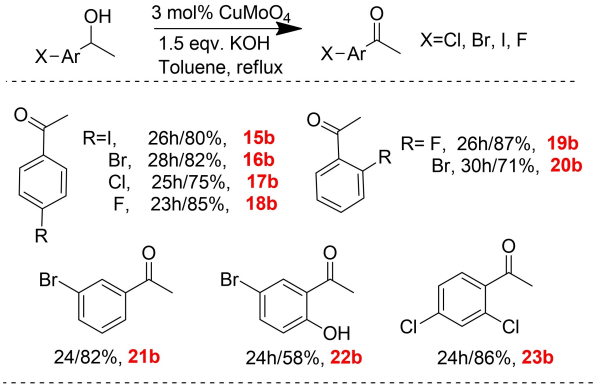
The $CuMoO_4$ bimetallic nanocatalyst is easily accessible and synthesized in gram scale by hydrothermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $CuCl_2\cdot 2H_2O$ aqueous solution in single step (for details see supp. Inf.).[18] At the start, we selected diphenyl methanol as model substrate for oxidation using $CuMoO_4$ nanocatalyst. A systematic screening of reaction condition revealed that the highest conversion of diphenyl methanol to benzophenone **1b** could be done in 95% yield with 5 mol% of catalyst in 24 h in presence of 1.5 eqv. of KOH by refluxing in toluene (Table 1, entry 2). Among the bases screened, stronger base such as K-O^{t}Bu (60%), NaOH (30%) afforded medium yield in comparison to other weak bases Cs_2CO_3, K_2CO_3, Na_2CO_3, (10-30%) (Table 1, entry 7–9), whereas pyridine, K_3PO_4, NEt_3 (Table 1, entry 10–12) did not afford any yield. Screening of solvents acetonitrile (80%), 1,4-dioxane (45%), dimthylformamide (55%) and *t*-BuOH (60%) under suboptimal condition found that CH_3CN could be a better solvent similar to toluene. Reducing temperature of recation increased reaction time and yield. However room temperature reaction did not afford any product. The overall oxidation selectivity is 100% without any side product.(for details see supp. Inf.).

Base concentration was very important for providing good yield. Use of 1 eqv. of KOH afforded only 70% of product without completion and lowering of base resulted diminished amount of product (Table 1, entry 3–6). However absence of base KOH did not gave any product (Table 1, entry 18). Next role of metal catalyst is investigated in the reaction. The reaction did not proceed in absence of $CuMoO_4$ nanocatalyst (Table 1, entry 17). However, under optimal condition; monometallic catalyst such as CuO and MoO_3 afforded only $<5\%$ of the oxidation products (Table 1, entry 19–20) as expected. This result anticipated that bimetallic nanocatalyst [Cu–O–Mo][21–22] is more superior than the monometallic catalyst. Refluxing the reaction with molecular oxygen (O_2) did not affect the reaction speed (table 1, entry 21). This hopeful result inspired that bimetallic $CuMoO_4$ nano-catalyst is capable of promoting alcohol oxidation without use of ligand, peroxide or additives.

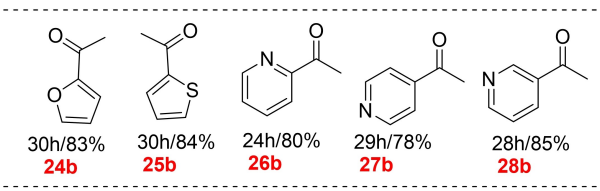
With the optimal conditions in hand, we examined the generality of the method for oxidation other substrates using $CuMoO_4$ nanocatalyst (Scheme 1–6). We investigated the reactivity of non-halogenated *ortho*-, *para*-, and *meta*-, substituted 1-aryl ethanol **2–14a** (Scheme 1). Para-substituted 1-phenyl ethanol, 1-(4-methyl phenyl) ethanol, 1-(4-ethyl phenyl) ethanol underwent oxidation to afford **2–4b** carbonyls compounds in 88–91% yield. Electron donating 1-(4-methoxy phenyl) ethanol and 1-(4-amino phenyl) ethanol afforded 79–93% **5–6b** yield. Similarly, *ortho*-substituted secondary aryl alcohols with electron donating groups such as 1-(2-methoxy phenyl) ethanol, 1-(2-amino phenyl) ethanol and 1-(2-hydroxy phenyl) ethanol underwent oxidation to corresponding ketone **7–9b** in 60–87% yield (Scheme 1). Meta-substituted 1-(3-amino phenyl) ethanol, and 1-(3-nitrophenyl) ethanol afforded 80–82% yield **10–11b** (Scheme 1). Under these condition, di-substituted 1-(3,4-dimethoxyphenyl) ethanol afforded oxidation product **12b** in



Scheme 1. Oxidation of secondary non-halogenated 1-aryl ethanol with $CuMoO_4$ nanocatalyst. [a] Alcohol (2 mmol), $CuMoO_4$ nano, catalyst (5 mol%, 11 mg), base (1.5 eqv.) were stirred in a 25 ml flask in 2 ml solvent under reflux condition, [b] Isolated yield.



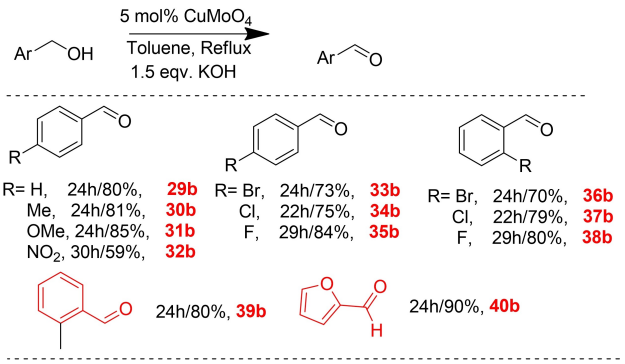
Scheme 2. Oxidation of halogenated secondary 1-aryl ethanol with $CuMoO_4$ nano-catalyst. [a] Alcohol (2 mmol), $CuMoO_4$ nano, catalyst (5 mol%, 11 mg), base (1.5 equ.) were stirred in a 25 ml flask in 2 ml solvent under reflux condition, [b] Isolated yield.



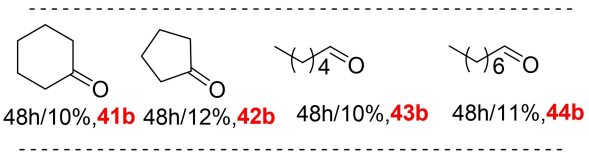
Scheme 3. Oxidation of 1-heteroarylethanol. [a] Alcohol (2 mmol), $CuMoO_4$ nano, catalyst (5 mol%, 11 mg), base (1.5 equ.) were stirred in a 25 ml flask in 2 ml solvent under reflux condition, [b] Isolated yield.

89% yield. 1-(naphthalen-2-yl) ethanol underwent oxidation in 88% yield of **13 b** after 28 h, whereas 1-(naphthalen-1-yl) ethanol afforded 83% oxidation product **14 b**. Electron donating substrates at aromatic ring works better than other substituent.

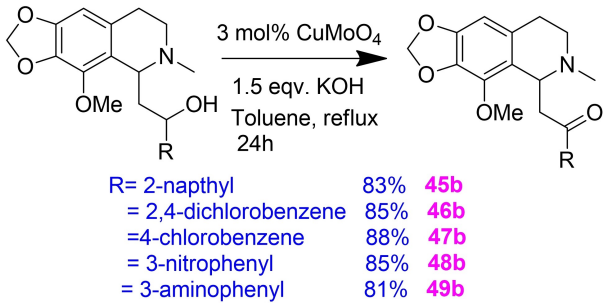
Subsequently, we focused on oxidation of halogenated 1-aryl ethanols with $CuMoO_4$ nanocatalyst. Para-substituted (4-bromo phenyl) ethanol, 1-(4-bromophenyl) ethanol, 1-(4-iodophenyl)ethanol, 1-(4-chlorophenyl) ethanol and 1-(4-fluoro phenyl) ethanol **15**–**18 a** were oxidised to corresponding ketone



Scheme 4. Oxidation of primary 1-arylmethanol with $CuMoO_4$ nanocatalyst. [a] Alcohol (2 mmol), $CuMoO_4$ nano, catalyst (5 mol%, 11 mg), base (1.5 equ.) were stirred in a 25 ml flask in 2 ml solvent under reflux condition, [b] Isolated yield.



Scheme 5. Scope of oxidation of aliphatic alcohol with $CuMoO_4$ nano-catalyst. [a] Alcohol (2 mmol), $CuMoO_4$ nano (5 mol%, 11 mg), base (1.5 equiv.) were stirred in a 25 ml flask in 1 ml solvent under reflux condition for 48 h, [b] Isolated yield.



Scheme 6. Application of oxidation reaction for synthesis important cotarnine based derivatives.

15–**18 b** in 75–85% yield (Scheme 2). The reactivity of *p*-substituted haloaryl alcohols follows the unusual reactivity with order 4-F > 4-Br < 4-I > 4-Cl. This is due to easy metal-bromine coordination and sterric congestion at ortho-position. 1-(2-fluoro phenyl) ethanol and 1-(3-bromo phenyl) ethanol afforded 71–87% yield of **19**–**20 b**. However it is note worthy that 1-(2-bromo phenyl) ethanol resulted the steric effect at *ortho*-position in comparison to 1-(3-bromophenyl) ethanol **21 b** in 82% yield. 2-hydroxy-3-bromophenyl ethanol afforded only 58% yield **22 b** after 24 h. 2,4-dichlorophenyl ethanol **23 a** underwent oxidation in 86% yield of **23 b** (Scheme 2).

With optimized reaction condition, we subsequently examined the generality of the method for a range of 1-heteroayl ethanols containing *O*-, *S*-, and *N*- atoms in the aromatic ring into the corresponding ketone (Scheme 3). For example, 1-(furan-2-yl)ethanol, 1-(thio furan-2-yl)ethanol, 1-(pyridin-2-yl)

ethanol, 1-(pyridin-3-yl) ethanol and 1-(pyridin-4-yl) ethanol **24**–**28 a** were successfully oxidised to corresponding ketone in 78–85% yield **24**–**28 b** within 24–30 h. The highest yields were obtained for 1-(pyridin-2-yl) ethanol among secondary hetero aryl alcohol (Scheme 3).[22]

Subsequently; oxidation of primary benzylic alcohols were investigated using $CuMoO_4$ catalyst under optimal condition (Scheme 4). Benzyl alcohol, 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol underwent oxidation to corresponding ketone **29**–**31 b** in 80–85% yield in comparison to 4-nitrobenzylalcohol in 59% yield (Scheme 4). Further, halogenated 4-bromo, 4-chloro-, and 4-fluoro benzyl alcohols were oxidised to corresponding aldehyde **33**–**35 b** in 73–84% of yield. 2-bromo, 2-chloro-, and 2-fluoro benzylalcohols underwent oxidation to corresponding aldehyde **36**–**38 b** in 70–80% yield. 2-methylbenzyl alcohol and furan-2-ylmethanol also underwent oxidation in 80–90% yield. It is note worthy that the oxidation stops at aldehyde stage without further oxidation to acids. *p*-nitrobenzyl affords medium yield in comparison to other primary aryl alcohols (Scheme 4).

The bimetallic $CuMoO_4$ nanocatalyst has been investigated further for oxidation of aliphatic secondary and primary alcohols. Secondary aliphatic alcohols such as cyclopentanol, cyclohexanol, 1-hexanol, and 1-octanol afforded **41**–**44 b** in 5–12% yield after 48 h (Scheme 5).

Application of $CuMoO_4$ bimetallic nanocatalyst is employed for the oxidation of synthetically important molecules having cotarnine skeletons of alkaloid family (Scheme 6).[22] Cotarnine derivativeshas very good anti-tussive and anticancer property. It is noteworthy that the oxidation reaction proceeded smoothly affording corresponding carbonyl products in 83–88% yield without any side product.[22c–d] The starting alcohols were synthesized by reduction of corresponding ketones with 2 eq. of $NaBH_4$ in 1 : 1 THF : EtOH (For details see supp. Information).

Catalyst is tested for 2 cycles after its recovery. There is no substantial decrease of reactivity, but the catalyst color is changed to dark black after first cycle. Surface UV spectroscopy revealed that there is change of structure during the reaction but the catalyst is recycled by wash with HCl followed by addition of KOH until pH = 8 (Figure 3) However we did not observe any leaching of metal catalyst as evident from high resolution mass spectra. The catalyst was employed ultimately for oxidation of **6 gm** of benzehydrol. We are pleased to find that the oxidation product benzophenone was isolated with 5.4 g (90%) yield after 72 h using 2.7 mol% of catalyst with TON = 293 and TOF 4 h^{-1} (for detail see supp. Info).

Plausible Mechanism and DFT calculations: As expected, Oxygen bridge might be executing electrical balance during oxidation process.[19–21,25–26] From the oxidation of series of compounds, it is observed that primary alcohols reacts faster in first four hour in comparison to secondary aryl alcohols and proceeds slowly afterward (see supp. Info.). However, aliphatic primary and secondary alcohols are reluctant for oxidation. The oxidation of alcohol is believed to be at copper centre due to its high reduction potential [Mo(+6), E = 0.11 mV); Cu(+2) E = 0.33 mV).[23–24] The DFT calculation also agreed that coordination of the deprotonated alcohol to the copper centre is favoured

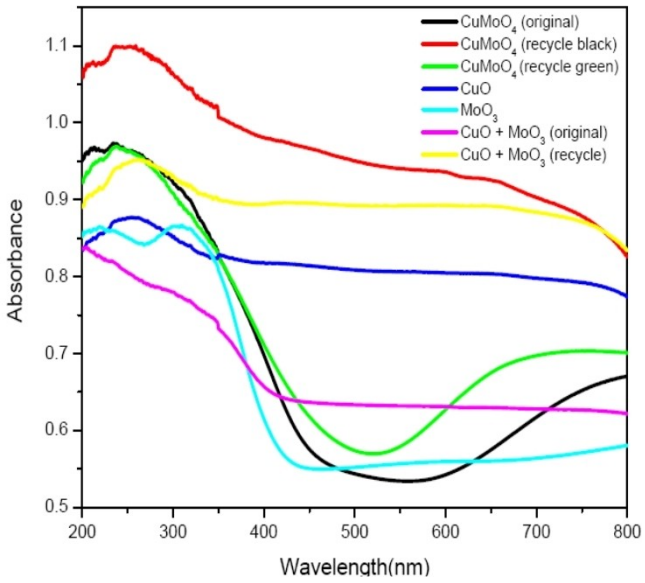


Figure 3. Surface UV of the catalyst; a) Original $CuMoO_4$ catalyst; b) $CuMoO_4$ catalyst after workup (red), c) Recycled $CuMoO_4$ catalyst at pH = 8 (green), d) CuO (blue), e) MoO_3 (light blue), e) CuO + MoO_3 1:1 intimate mixture (pink), f) CuO + MoO_3 1:1 intimate mixture (yellow).

over the molybdenum centre by ≈24 kcal/mol for both cyclohexanol and 1-phenyl ethanol (See supp. Info).[27–28]

An dehydrogenative oxidation mechanism is believed to occur.[29] We tried to trap H_2 if evolved, during the oxidation reaction due to dehydrogenation mechanism. But the evolved gas from the 5 mmol oxidation reaction vessel to the flask containing 1 mmol of styrene in presence of Pd/C in methanol did not afford any reduction product; that may probably due to low pressure of evolved H_2 gas (For details experimental set up, see supp. Info.). So we are not able to conclude the evolution of H_2 gas during the reaction.

Computational DFT study of $CuMoO_4$ catalyst with 1-phenyl ethanol reveals that the alcohol oxygen is coordinated and oxidised at copper centre instead of molybdenum (Scheme 7). the anion of alcohol forms complex **B** with catalyst **A** with $\Delta G_{A-B} = -20.3$ Kcal/mol. The complex **B** could be sliding over to π-stabilized complex **C** with $\Delta G_{C-B} = -36.4$ cal/mol (Figure 4). The complex **B** is transformed to **D** with $\Delta G_{B-D} = -12.3$ Kcal/mol and coordinate to the oxygen in presence of base KOH. Complex **D** could be transferred directly to **F** (G_{D-F} =

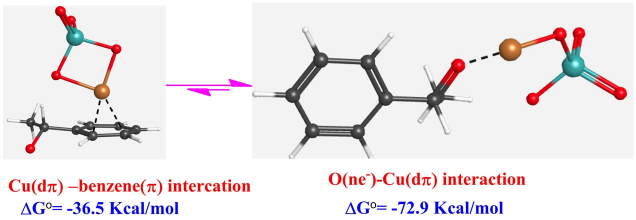
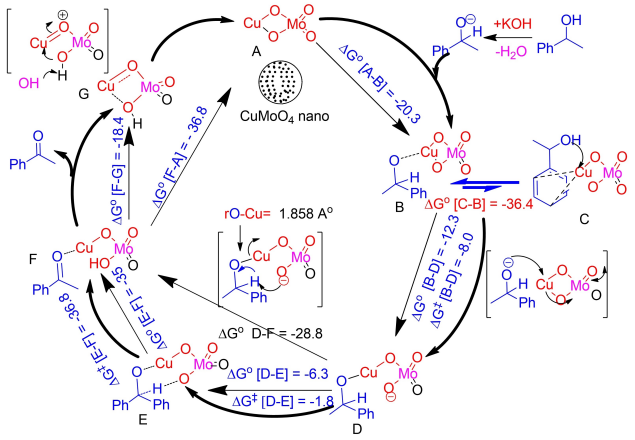


Figure 4. Cu(dπ)-benzene(π) interaction versus O (non-bonding electron)-Cu(dπ) interaction energy for copper coordinated transition state of $CuMoO_4$ with 1-phenyl ethanol. Rel. G (kcal/mol) using M06L/6-31G(d)/auto, Orange = Cu, Blue = Mo, Red = O, Black = C and White = H.



Scheme 7. Proposed mechanism for alcohol oxidation by $CuMoO_4$; usinh Single point calculations of copper coordinated interaction energy in $CuMoO_4$ in 1-phenyl ethanol; (Rel. G (kcal/mol) using M06L/6-31G(d)/auto, Orange = Cu, Blue = Mo, Red = O, Black = C and White = H.

−28.8 Kcal/mol) or via intermediate **E** (G_{D-E} = −6.3Kcal/mol). Subsequent dehydrogenation from **F** results formation of product and recycle of catalyst $CuMoO_4$ (Scheme 7).[29] The difference in the catalytic activity of monometallic CuO and MoO_3 catalyst could be realized from table 1(entry 2, 19&20) in comparison to bimetallic [**Cu**–**O**–**Mo**] moiety. The interaction barrier energy of monometallic CuO and MoO_3 catalyst is much higher than bimetallic $CuMoO_4$. The mechanism for the monometallic species CuO and MoO_3 were also studied with oxidation of 1-phenyl ethanol. They were found to have much larger barrier heights for hydrogen transfer than the bimetallic $CuMoO_4$ (11.7 kcal/mol) with 31.5 kcal/mol for CuO and 40.3 kcal/mol for MoO_3.

In conclusion, we have developed dehydrogenative benzylic alcohol oxidation with novel oxygen bridged bimetallic $CuMoO_4$ nanocatalyst for first time. The [**Cu**–**O**–**Mo**] nanocatalyst is able oxidize a diverse array of primary and secondary aromatic and hetero aromatic benzylic alcohols to corresponding carbonyl compounds without over oxidation and good functional group tolerance. The concept also strongly supported by detailed DFT study. In addition to our previous concept and report,[19] oxygen bridged bimetallic catalyst [M–O–M], will surely open an new direction in organic synthesis.

Experimental Section

Benzyhydrol Oxidation in 6 g scale: A oven dried 100 ml flask was equipped with a magnetic stirring bar. To 6 g (32.5 mmol) of benzehydrol, 199 mg (2.7 mol%) of catalyst $CuMoO_4$ nano, KOH (2.73 g, 1.5 eqv.) and 50 ml of toluene is refluxed. The reaction was stopped after 72 h. The reaction mixture was cooled and concentrated in rotor under reduced pressure. The residue was purified by flash column chromatography (ethylacetate and hexane) to give the corresponding carbonyl compound in 90% yield (5.3 g) as white solid. ^{1}H $CDCl_3$ (400 MHZ): δ 7.82 (d 4H, J = 8 Hz), 7.59 (dd, 2H, J = 4 Hz, 8 Hz), 7.49 (t, 4H, J = 8 Hz); ^{13}C $CDCl_3$ (100 MHZ): δ 196.7, 135.57, 132.39, 130.03, 128.25.

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Conflict of Interest

The authors declare no conflict of interest.

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