New findings for the oxidation of alcohols in the presence of a copper complex were reported.
New findings and current controversies on oxidation of benzyl alcohol by a copper complex

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Abstract

Herein, we report the new findings and details for the alcohol-oxidizing activity of a copper complex in the presence of molecular oxygen. Using scanning electron microscopy, transmission electron microscopy, UV-vis spectroscopy, Fourier transform infrared spectroscopy, X-ray absorption near edge structure, extended X-ray absorption fine structure, and X-ray diffraction, it is suggested that the true catalyst for the reaction is a copper complex mixed with potassium carbonate.

KEYWORDS: Copper(II) complex, oxidation of alcohols, true catalyst, Cu(II) phenanthroline, Marko’s complex
Introduction

The oxidation of alcohols to carbonyl compounds is an important reaction, which is done typically by permanganate and dichromate salts. These salts are moderately corrosive, unstable, expensive, toxic and show no selectivity. These salts also require hazardous procedures for the preparation and over-oxidation to carboxylic acids is observed in the presence of these oxidants. For the first time, Semmelhack's group used CuCl (10 mol%) and TEMPO (10 mol%) to oxidize primary alcohols in the presence of molecular oxygen at room temperature.\(^\text{[1]}\) In 1996, Marko’s group reported an efficient copper-based catalyst that oxidized many alcohols into aldehydes and ketones under mild conditions.\(^\text{[2]}\) The true catalyst under Marko’s conditions is suggested to be a heterogeneous and adsorbed compound on K\(_2\)CO\(_3\). Such oxidation reactions have been performed by many copper complexes with different ligands.\(^\text{3-42}\)

Marko’s group proposed that an initial hydrogen-transfer reaction within the copper-alkoxide/azo complex generates the carbonyl-bound hydrazino-copper species, which produces a binuclear copper(II) peroxide upon reaction with oxygen. After the homolytic cleavage followed by a hydrogen atom, the hydroxy Cu(I) complex is formed (Scheme 1). The rapid exchange between the OH ligand and the alcohol regenerates the catalyst (Scheme 1).

The clear role of K\(_2\)CO\(_3\) or the true catalyst is not known, however, some points and questions are:

i) HCl is formed during this reaction. K\(_2\)CO\(_3\) is a base and could react with HCl.

ii) K\(_2\)CO\(_3\) is a support.

iii) K\(_2\)CO\(_3\) could act as a water scavenger.

iv) What is the role of K\(_2\)CO\(_3\)?

v) What is the true catalyst: Marko’s complex, Cu(II) complex, CuCl\(_2\), or CuCl?

vi) What is the nature of dark copper-based compound on the K\(_2\)CO\(_3\)?

The finding of the true catalyst is important to design and synthesize new, stable, and efficient catalysts. In 2010, Liang et al. reported a procedure using the “copper(II) chloride-cesium carbonate”...
to aerobically oxidize primary alcohols.\textsuperscript{43} \( \text{Cs}_2\text{CO}_3 \) and the solvents such as toluene and 1,2-dichloroethane play important roles to form a catalytically active intermediate containing a hydroxyl-bridged trinuclear copper moiety. From the X-ray crystal structure of trinuclear copper, an electrostatic interaction between \( \text{Cl}^- \) and \( \text{Cs}^+ \) was observed, which stimulated to suggest the roles of \( \text{Cs}_2\text{CO}_3 \) in this reaction as a base, stabilizing and “solvating” intermediates in toluene and 1,2-dichloroethane.\textsuperscript{43}

In this study, we report new findings for the alcohol-oxidizing activity of a Cu complex in the presence of molecular oxygen. Herein, using scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and X-ray diffraction (XRD), it is proposed that the true catalyst for the alcohol oxidation in the presence of Marko’s complex is a mixture of the copper complex and potassium carbonate particles than nanosized copper oxide or copper carbonate.

\begin{center}
\textbf{Scheme 1} The proposed mechanism for the alcohol oxidation by Marko’s complex. The role of diethylazodicarboxylate is the reduction of the copper(II) complex and the formation of the copper(I) complex. The image is modified from ref. 2.
\end{center}
Experimental

Materials and methods

See Supporting Information.

Synthesis of complex

1 was prepared by the reaction of 1,10-phenanthroline (Phen) monohydrate (0.40 g, 2.0 mmol) and Cu(ClO$_4$)$_2$·6H$_2$O (0.37 g, 1.0 mmol) in 30.0 mL of acetonitrile at room temperature (Figure 1).\textsuperscript{44}

2 was synthesized by the reaction of Cu(ClO$_4$)$_2$·6H$_2$O (0.37 g, 1 mmol) and Phen (0.20 g, 1 mmol) in acetonitrile (40.0 mL) (Figure 1).\textsuperscript{45}

![Figure 1 Schematic structures of 1 and 2](image)

Catalytic procedure

The catalytic activity of 1 in the alcohol-oxidation reaction

The alcohol-oxidation procedure by 1 or 2 was carried out in an oxygenic atmosphere at 80 °C.

In a typical experiment, diisopropyl azodicarboxylate (DIAD; 5 mmol%), benzyl alcohol (1.0 mmol), 1 or 2 (5.0 mmol%), and K$_2$CO$_3$ (0.27 g, 2.0 mmol) were stirred in 5.0 mL of oxygen saturated toluene in a 10.0 ml two-neck round-bottom flask equipped with an oxygen balloon.

The solution was stirred at 80 °C for 90 min.
Results and Discussion

Recently, some studies have addressed the mechanism of oxidation by Marko’s complex. However, more investigation on a true catalyst for this reaction is essential. A question is whether Cu(II) complexes by Phen ligands are active for the oxidation of benzyl alcohol to benzaldehyde under Marko’s conditions or not. The oxidation of benzyl alcohol to benzaldehyde using K$_2$CO$_3$ as both base, and 1 as the catalyst, was selected as the model reaction following Marco’s report in 1996. [Cu(Phen)$_2$CH$_3$CN(ClO$_4$)$_2$] (1) was simply obtained by the reaction of 1, Phen and Cu(ClO$_4$)$_2$ in a 1:1 ratio, and blue-green crystals were grown in CH$_3$CN. The crystal structure of 1 comprises two Phen ligands and one acetonitrile coordinated to Cu$^{II}$ lying in a distorted square-pyramidal geometry (Figure 1). [44,45]

First, Marco’s reaction was performed (Scheme 2a). As previously reported, the formation of a dark solid adsorbed on the K$_2$CO$_3$ was observed, and the alcohol oxidation was detected. 2 was inactive for the alcohol-oxidation reaction. However, 1 indicated the alcohol-oxidizing activity in the presence of molecular oxygen (Scheme 2b) according to Marko’s report.

![Scheme 2](image)

**Scheme 2** The schematic conditions of the alcohol-oxidation reaction Marco’s reaction (a) and in the presence of 1 under Marco’s reaction conditions (b).

First, the color of the solution of 1 in toluene is light green, but after 45 minutes under conditions similar to Marko’s conditions (Scheme 2b), the color turns dark (Figure S1, ESI†). The profile of the reaction was monitored by gas the chromatography (Figure 2). In the first 45 min, the alcohol-oxidation reaction is slow, but after the formation of a dark solid, an increase in the activity was
observed. The highest yield of benzaldehyde ( ~23%) was measured after 90 min. An important question in this regard is that whether the dark solid is a true catalyst or a product of decomposition? The obtained dark precipitation was separated, rinsed three times with toluene, and resuspended in toluene and benzyl alcohol (BnOH) in the presence of O₂ at 80 °C (Figure 2). Immediately, the benzaldehyde formation was observed, and the yield was 38% at 90 min. The result showed that this dark precipitate could perform the alcohol-oxidation reaction as a catalyst (Figure 2). As shown in Table S1, CuO in the presence and absence of Phen could not oxidize benzyl alcohol.

![Graph showing benzaldehyde formation](image)

**Figure 2** The reaction profiles of benzaldehyde formation by 1 and the centrifuged nanoparticles from the reaction of 1. The dark circle showed the time for the dark solid.

As shown by Marko,[2] azo compounds, such as diethyl azodicarboxylate or its analog significantly improve the turnover for the alcohol oxidation, the lifetime of the catalyst, and also the rate of the reaction. The role of DIAD is the reduction of the copper(II) complex and the formation of the copper(I) complex.

2 was not a catalyst under Marko’s conditions (Table 1; for a completed table see Table S1, Entry 2), but 1 (Entry 3) or the centrifuged nanoparticles from the reaction of 1 (solid 1) showed the activity for the alcohol-oxidation reaction (Entry 4). Replacing CuCl by Cu(ClO₄)₂ in Marko’s reaction resulted in low activity for the alcohol-oxidation reaction (Entry 5). No activity was observed in the presence of CuCl or CuI but in the absence of Phen (Entry 6 and 7). Cul in the presence of Phen indicated a high activity toward the alcohol-oxidation reaction (Entry 8). K₂Cu(CO₃)₃ or CuCO₃ in both the presence or absence of Phen could not oxidize benzyl alcohol.
performed the alcohol-oxidation reaction using other bases such as Na$_2$CO$_3$ and Cs$_2$CO$_3$, where the conversions of benzyl alcohol were the same. However, a poor conversion was achieved using Et$_3$N. These results suggest that the mixing catalyst with K$_2$CO$_3$ plays an important role to increase the reactivity of copper complex in the alcohol oxidation.
Table 1 benzyl alcohol oxidation by the catalyst, and the centrifuged nanoparticles from the reaction

| Entry | Catalyst | Benzyl alcohol (%) | Benzaldehyde (%) | Conditions |
|-------|----------|--------------------|------------------|------------|
| 1     | CuCl     | 22                 | 78               | CATAL (5%), PHENANTHROLINE (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 2     | Complex (2) | 99-95         | 1-5              | CATAL (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 3     | Complex (1) | 75              | 25               | CATAL (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 4     | Centrifuged solid from the reaction of entry 1 | 62              | 38               | CATAL (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 5     | Cu(ClO₄)₂ | 85                 | 15               | CATAL (5%), PHENANTHROLINE (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 6     | CuCl     | 99-95             | 1-5              | CATAL (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 7     | Cul      | 99-95             | 1-5              | CATAL (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |
| 8     | Cul      | 22                 | 78               | CATAL (5%), PHENANTHROLINE (5%), DIAD (5%), K₂CO₃ (2 eq), Toluene (5 ml), 80 °C, O₂, 90 min |

Afterward, the obtained dark solid under the alcohol-oxidation reaction by 1 was analyzed by SEM, TEM, EDX, and XRD analyses.
The SEM images of the obtained dark solid (solid 1) displayed nanoparticles without any especial morphology in the average size of 30~200 nm (Figure 3a, Figure S3, ESI†). Both crystalline and amorphous particles could be detected in SEM images. These two types of particles were significantly aggregated. According to XRD patterns, the crystalline particles could be both K$_2$CO$_3$·1.5 H$_2$O and 1 (Figure 3b). Based on the EDX data, in addition to O and C, the obtained solid contained Cu and Cl (Figures 3b and 3c).
Figure 3 SEM images (a,b), EDX spectrum (c) and EDX results for two points (d). DLS (e) of solid 1 under Marko’s conditions. Yellow and blue arrows shows two different morphologies.

90 min after the reaction of 1 with K₂CO₃, the formed particles were separated and investigated by dynamic light scattering (DLS). DLS in water indicated the diameter ~100 nm for the nanoparticles. Compared with particles in SEM or TEM images, different sized particles were observed in DLS analysis (Figure 3e). K₂CO₃ is soluble in water, and thus, only Cu-containing particles could be investigated by DLS.

TEM of solid 1 showed two different particles: K-containing particle (light particles) and Cu-containing particles (dark particles) (Figure 4a). As shown by SEM images, these two types of particles were significantly aggregated. Although, in Marko’s report, it was suggested that the active catalyst is a heterogeneous catalyst supported on the K₂CO₃. TEM images confirmed the presence of nanoparticles in the size range (50-200 nm) (Figure 4a). As can be seen, dark nanoparticles (ca. 100 nm) are dispersed among big light particles (Figure 4b; Figure S4-S7, ESI†). Thus, TEM images similar to SEM images showed a mixture of Cu and K-containing particles for solid 1 under Marko’s conditions.

HRTEM image of solid 1 showed non-crystallinity of nanoparticles (Figure 4c), but in a few areas, the patterns with a d-spacing of 0.27 nm (Figure 4c) corresponded to planes in range 2θ: 30-33° for 1 or K₂CO₃ and in agreement with the powder X-ray diffraction (XRD) pattern were observed.
Figure 4 TEM (a) and (HR)TEM (b,c) of solid 1 under Marko’s conditions. Scale bars in image c is 5 nm.

In FTIR spectra for 1 and solid 1, some peaks at 1400-1600 cm\(^{-1}\) were observed that are attributed to C=N/C=C, suggesting the intact structure of 1 (Figure 5). The FTIR spectrum of phenanroline showed the stretching vibration peaks of C=N and C=C double bonds at 1643 cm\(^{-1}\) and 1583 cm\(^{-1}\) and the skeleton vibration peak at 1555 cm\(^{-1}\), and the out-plane bending vibration peak of C-H bond appears at 734 cm\(^{-1}\). Compared with the spectrum of the phenanroline, the stretching vibration peaks for 1 was observed at 1626 (C=N) and 1584 (C=C) cm\(^{-1}\). The out-plane bending vibration peak of C-H bond also shifts from 735 cm\(^{-1}\) in the phen to 720 cm\(^{-1}\) in the complex. After reaction, FTIR spectrum of solid 1 showed the related peaks at 1620 and 1583 cm\(^{-1}\) attributed to
C=N and C=C double bonds in metal complex. The out-plane bending vibration peak of C-H bond was also observed at 720 cm\(^{-1}\).\(^{47}\) Thus, FTIR experiment showed that copper complex in solid 1 intact.

Marko’s group also reported that the solution obtained from filtration of the heterogeneous mixture was devoid of any oxidizing ability. Conversely, the obtained precipitate indicated the activity for the oxidation reaction.

![IR spectra](image)

**Figure 5** IR spectra of Phen (a), 1 (b) and solid 1 after a few second (c) and after 90 minutes (d) under Marko’s conditions at different range.

The XRD patterns also showed the presence of Cu(Phen) based-material on K\(_2\)CO\(_3\) (**Figure 6d** and **6e**). It seems that Marko’s conditions highly depends on forming Cu(Phene) in the presence of K\(_2\)CO\(_3\). When K\(_2\)CO\(_3\) was added after Cu(Phen) forming, the conversion of benzyl alcohol was achieved in lower yield (35% in 90 min).
Figure 6 XRD patterns for 1 (a), K$_2$CO$_3$·1.5H$_2$O (ref. code: 00-011-0655) (b), and solid 1 under Marko’s conditions (c). The obtained solid from the mixing of CuCl and Phen after 30 min (* is related to CuCl (ref. code: 01-077-2383)) (d). The obtained solid from the mixing of CuCl, Phen, K$_2$CO$_3$, DIAD, and BnOH after 90 min (Marko’s report) (e).

To further characterize the solid, the XANES spectra were used. Figure 7 illustrates the normalized XANES spectra along with derivative spectra (Figure 7b) of various compounds.

Figure 7 XANES (a) and the first derivative curve (b) for different compounds.
The main edge of the dark obtained compounds at the reaction of complex 1 and 2 and solid 1 and 2, respectively, along with various materials appear at higher energy than CuO. This reveals that the valence state of Cu ions is higher than that of 2. However, this shift is also associated with the presence of the ligand in the complex organic systems.\textsuperscript{48, 49} Thus, the ligand effect may be one of the reasons for the higher energy shift in these complex systems. The first derivative curve also exhibits a similar effect (Figure 7b). To get the information of bond distances for these materials, these spectra were simulated using a quick shell parameter fit. The fitted inverse Fourier transform of EXAFS spectra are shown in Figure 8a. The values of coordination number, N, and radial distance, R, are shown in Figure 8b.

![Figure 8](image)

**Figure 8** Inverse Fourier transform spectra of various materials along with oxides (a); coordination number and radial distances for different materials (b).

Both the experimental and fitted data points are in agreement in the fitting range. The values of coordination number and radial distances for the Cu-O shell for oxides like CuO and Cu\textsubscript{2}O are similar to that of reported values. In the case of solids 1 and 2, the values of radial distances are 1.94±0.01
and 1.938±0.006Å, respectively, with coordination numbers being 4.5±1.0 and 4.7±0.7, respectively. However, compared to previous reports, Cu-O bonds occur at 2.433 Å with a coordination number of 2 for solid 2. Cu ions are surrounded by 4 N ions bonds having average bond distance ~ 1.98 Å, which are comparable to the values estimated for solids 1 and 2 (Figure 8b). Thus, these materials contain Cu-N bonds. Based on the above observations, we infer that the true catalyst is Cu complex mixed with K$_2$CO$_3$.

Finally, a question posed to Mako’s catalyst is why such a system in the presence of a strong base is not efficient for alcohol oxidation. A simple experiment indicated that copper complexes with one Phen ligand such as 2 were simply decomposed or dimerized in the presence of KOH or NaOH (Figure S4, ESI†). As we showed that a molecular structure is an active species in Marko’s system, it is not surprising that strong bases such as KOH or NaOH are not appreciated under Marko’s conditions. However, the alcohol-oxidation reaction is usually very complicated and other factors could be also important.$^{54,55}$

**Conclusions**

Using SEM, TEM, UV-vis spectroscopy, FTIR, XANES, EXAFS, and XRD analyses, we conclude that a Cu molecular-based complex is a true catalyst for the alcohol-oxidation reaction under Marko’s conditions in the presence of molecular oxygen. In the presence of K$_2$CO$_3$ and 1, a solid was observed. Characterization of the solid showed that it is Cu(II) complex mixed with K$_2$CO$_3$. It seems that the heterogeneous catalysts are more complicated than we think before.

According to our experiments:

i) Cu(I) than Cu(II) is critical for the reaction.

ii) Phen is important for the reaction.

iii) The stable salts such as CuCO$_3$, CuO and K$_2$Cu(CO$_3$)$_2$ showed no activity.

iv) The active catalyst was mixed with K$_2$CO$_3$.  

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v) In Marko’s conditions, a Cu(I) complex in the presence of oxygen is oxidized to Cu(II). It is suggested that the adduct is produced by the reaction of oxygen and Cu(I) complex for the alcohol-oxidation reaction because a Cu(II) complex such as 1 or 2 is not highly active under Marko’s conditions.

vi) Nanosized K$_2$CO$_3$ significantly mixed with the complex.

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**Competing financial interests**

The authors declare no competing financial interests.

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