# Cu precipitate formed during the benzene oxidation catalyzed by supported Cu in the presence of ascorbic acid and O$_2$

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## Abstract

The composition of the Cu precipitate formed during the liquid-phase oxidation of benzene to phenol with the Cu catalyst in the presence of O$_2$ and ascorbic acid was investigated in order to clarify the cause of the deactivation of the Cu catalyst. The elementary analysis, the IR spectrum, and the XRD pattern of the Cu precipitate were measured in order to elucidate the composition and the structure. The formed Cu precipitate was confirmed to be a Cu oxalate analogue (Cu[OC(=O)C(=O)OH]) based on the similarities of its IR spectrum, XRD pattern, and the elemental analysis with those of copper oxalate. The Cu precipitate was not formed in the absence of ascorbic acid and/or O$_2$. The Cu/ascorbic acid mole ratio affected the formation of the Cu precipitate. The time dependence of the formation of the Cu precipitate revealed that the Cu oxalate analogue was first produced via the cuprous oxide and then the copper metal.
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## 1. Introduction

The one-step synthesis of phenol through the benzene oxidation using gaseous oxygen is one of the most attractive oxidation reactions, though the direct oxygenation of benzene is very difficult due to the stability of benzene ring. Not only from an organic synthetic point of view, but from a practical point of view, the phenol production via the one-step process using gaseous oxygen is of interest, in spite of the established cumene process which includes a three-step scheme and accompanies the production of acetone as a byproduct. The pioneering approach for the liquid-phase direct synthesis of phenol is the liquid-phase benzene oxidation using the ferric sulfate–H$_2$O$_2$ system (Fenton reagent) by Dixon and Norman [1]. The partially exchanged hetero-poly acid was more recently reported as a catalyst for the liquid-phase oxidation of benzene in the presence of H$_2$O$_2$ oxidant [2,3]. We have also

reported the liquid-phase oxidation of benzene catalyzed by supported Cu [4–7] catalysts using both gaseous oxygen and ascorbic acid as an oxidant and a reducing reagent, respectively. However, a drawback in the supported Cu-ascorbic acid-O$_2$ catalytic system is that the catalytic activity for phenol formation stops during the initial stage of the oxidation [6,7]. Part of the Cu species on the supported Cu catalyst was observed to leach into the reaction solution during the initial stage of the phenol formation [8]. The eluted Cu species once again rapidly precipitated followed by deactivation of the phenol formation [8]. The amount of Cu precipitate has been reported [9] to be correlated to the yield of phenol, thus the precursor of the Cu precipitate is thought to be an active Cu species for the benzene oxidation to phenol. The irreversible formation of the Cu precipitate is thus suggested to be a cause of the deactivation during phenol formation [8].

The purpose of this study is to shed light on the composition and the structure of the Cu precipitate, of which the resolved Cu species are thought to be active for the benzene oxidation, formed from the aqueous solution of copper ac-

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etate and ascorbic acid in the presence of $O_2$ to elucidate the cause of the rapid deactivation [6,7] of the supported Cu catalyst in the presence of both ascorbic acid and $O_2$.

## 2. Experimental

### 2.1. Preparation of catalyst

A Cu catalyst ($Cu/Al_2O_3$) supported on $Al_2O_3$ (JRC-ALO-6) was prepared by a conventional impregnation method using an ethanolic $Cu(OCOCH_3)_2 \cdot H_2O$ (Nacalai tesque, guaranteed reagent) solution followed by drying at 393 K overnight and calcining at 773 K for 5 h in flowing air.

### 2.2. Liquid-phase oxidation of benzene

Benzene (Nacalai tesque, guaranteed reagent) was used without further purification after checking the impurity by GLC. Both acetic acid (Nacalai tesque, guaranteed reagent) and ascorbic acid (Nacalai tesque, guaranteed reagent) were used as received. The liquid-phase oxidation of benzene was carried out in a $50\,cm^3$ flat-bottomed flask, in which $2\,cm^3$ (22.5 mmol) of benzene in $20\,cm^3$ of aqueous acetic acid solvent, 0.7 g (4 mmol) of ascorbic acid and 0.4 g of catalyst were mixed using a magnetic stirrer at 303 K under an $O_2$ atmosphere (0.1 MPa). The oxidation product, after separating the solid catalyst by the centrifugation of the reaction solution, was analyzed by a GLC (Shimazu, model GC-8A) equipped with a 3 m stainless-steal column filled with silicon OV-17 at 463 K.

### 2.3. Preparation of Cu precipitates

The prescribed amounts of aqueous acetic acid, $Cu(OCOCH_3)_2 \cdot H_2O$, and ascorbic acid were mixed using a magnetic stirrer in a $50\,cm^3$ flat-bottomed flask at 303 K for 24 h under an $O_2$ atmosphere (0.1 MPa). The resulting Cu precipitate was filtered off, washed with acetone and dried at 393 K overnight.

### 2.4. XRD measurement of the Cu precipitates

The XRD patterns of the Cu precipitates were observed at room temperature using a Rigaku RINT 2000 XRD instrument with a Cu Kα source. The XRD patterns of the Cu powder, $Cu_2O$, $CuO$, $Cu(OCOCH_3)_2 \cdot H_2O$, and $Cu(OCCO)_2$ were also measured as references.

### 2.5. FT-IR measurement of the Cu precipitates

The FT-IR spectra of the Cu precipitates, together with various known Cu species, were measured using a Nihon Bunko VALOR-III spectrophotometer. After approximately 10 mg of sample was mixed with about 200 mg of KBr in an agate

mortar, the entire sample was pressed at about $400\,kg/cm^2$ to form a 20-mm diameter disk.

### 2.6. Elementary analysis of the Cu precipitates

The elementary (C, H) analyses of the Cu precipitates were carried out using a Yanako type CHN CORDER MT-5 instrument. All the samples were dried overnight at 393 K before the analysis.

## 3. Results and discussion

The liquid-phase oxidation of benzene catalyzed by Cu catalysts supported on various inorganic oxides such as $Al_2O_3$ and/or HY using both gaseous oxygen and ascorbic acid as an oxidant and a reducing reagent, respectively, selectively produced [4–7] an oxygenated product, phenol. Though the yield of phenol increased with the reaction time during the initial reaction stage, the extent of the phenol increase significantly decreased beyond the reaction time of about 5 h, irrespective of the supported Cu catalysts [6,7].

### 3.1. XRD pattern of the Cu precipitate

A new XRD peak appeared [8] at around $2\theta = 23°$ in the XRD pattern of the used $Cu/Al_2O_3$ catalyst, after the liquid-phase benzene oxidation at 303 K for 24 h (the phenol yield: 2.1%) (Fig. 1). The XRD peak at $2\theta = 23°$ was not identical to that of the copper acetate, a Cu precursor of the $Cu/Al_2O_3$ catalyst or the ascorbic acid as the reducing reagent. The broad XRD peaks observed at around $2\theta = 37$ and $45°$ are attributed to the $Al_2O_3$ support.

To avoid the appearance of the concomitant XRD peaks based on the oxide support, the preparation of the pure Cu precipitate was attempted at 303 K for 24 h to directly isolate using both copper acetate (0.125 mmol) and ascorbic acid (4 mmol) in aqueous solvents ($20\,cm^3$) of 80 and 40 vol.% acetic acid, and also in a pure $H_2O$ solvent without acetic acid under air atmosphere. The XRD pattern of the Cu pre-
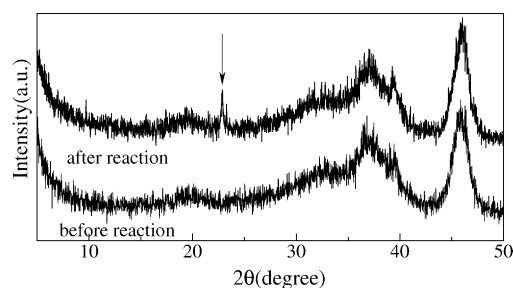


Fig. 1. XRD patterns of both the fresh and used $Cu(2)/Al_2O_3$ (Cu; 2 wt.%) catalysts. Used catalyst; washed with acetone and dried at 393 K overnight after the benzene oxidation (reaction conditions: $Cu(2)/Al_2O_3$ catalyst, 0.4 g; benzene, $2\,cm^3$; solvent, $20\,cm^3$ of aqueous solution of 80 vol.% acetic acid; ascorbic acid, 4 mmol; $O_2$, 0.1 MPa; reaction time, 24 h; reaction temperature, 303 K).
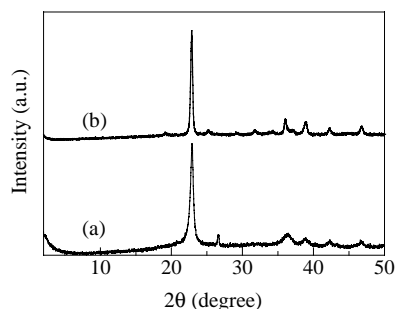
Fig. 2. XRD patterns of the Cu precipitate and Cu oxalate: (a) Cu precipitate; preparation conditions: Cu acetate, 0.125 mmol; 20 cm³ of aqueous solvent of 80 vol.% acetic acid; $O_2$; 0.1 MPa; ascorbic acid, 4 mmol; reaction time, 24 h; reaction temperature, 303 K; (b) Cu oxalate.

cipitate formed in an aqueous solvent of 80 vol.% acetic acid, appearing as one main peak at $2\theta$ = around 23°, is illustrated in Fig. 2(a). These XRD patterns of the Cu precipitates prepared in the different solvents were entirely different from those of Cu acetate and/or ascorbic acid (figure not shown). Since the XRD peak of the Cu precipitate was found to be similar to that of the Cu oxalate using the XRD database, the XRD pattern of authentic Cu oxalate (Fig. 2 (b)) was observed and compared with that of the Cu precipitate (Fig. 2 (a)). The main XRD peaks appeared at $2\theta$ = 23° for the isolated Cu precipitates and Cu oxalate were basically identical, though the intensities of the XRD peaks of the Cu precipitate prepared in an aqueous solvent containing more acetic acid tended to become lower and broader (Fig. 3).

## 3.2. IR spectra of the Cu precipitate

The FT-IR spectra of both the Cu precipitate and Cu oxalate were observed to further investigate the structure of the isolated Cu precipitate (Fig. 4). Both IR spectra almost coincided except in the region of 3500–3000 cm$^{-1}$. The IR peak at around 1650 cm$^{-1}$, the two sharp peaks at 1400–1350 cm$^{-1}$, and the one sharp peak at 820 cm$^{-1}$ are identified as a C=O stretching, C–O and C–C stretching, and O–C=C bending frequencies, respectively. These IR peaks are thought to have
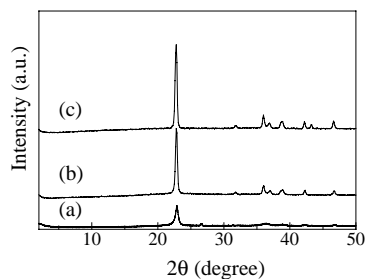


Fig. 3. XRD patterns of the Cu precipitates prepared in aqueous solvent with different acetic acid concentrations. Preparation conditions of the Cu precipitate: Cu acetate, 0.125 mmol; 20 cm³ of aqueous solvent with different acetic acid; $O_2$, 0.1 MPa; ascorbic acid, 4 mmol; reaction time, 24 h; reaction temperature, 303 K: (a) 80 vol.% acetic acid; (b) 40 vol.% acetic acid; (c) $H_2O$ (0 vol.% acetic acid).
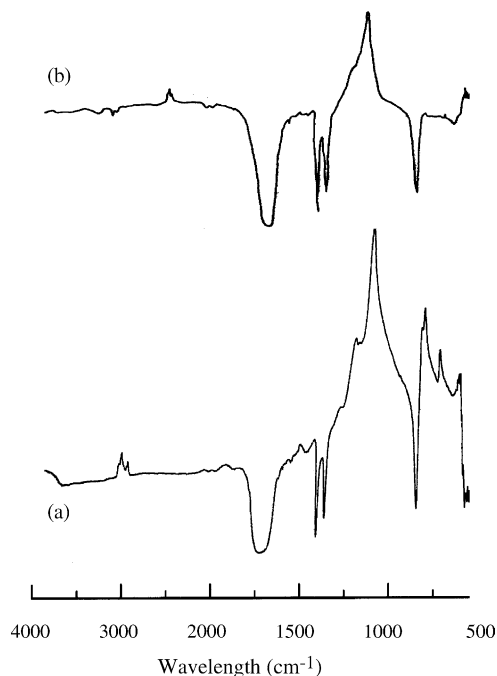


Fig. 4. IR spectra of the Cu precipitate and Cu oxalate. Preparation conditions of the Cu precipitate; Cu acetate, 0.125 mmol; 20 cm³ of aqueous solvent of 80 vol.% acetic acid; $O_2$; 0.1 MPa; ascorbic acid, 4 mmol; reaction time, 24 h; reaction temperature, 303 K: (a) Cu precipitate; (b) Cu oxalate.

originated from the oxalate group. A broad peak at around 3600 cm$^{-1}$ appeared in the IR spectrum of the Cu precipitate (Fig. 4 (a)), of which a band not appearing in the IR one of the Cu oxalate (Fig. 4 (b)), may be OH stretching of a COOH group of oxalic acid. All the obtained IR and the previous XRD data support the fact that the isolated Cu precipitate includes the oxalate moiety.

## 3.3. Elemental analysis (C, H) of the Cu precipitate

The C, H analyses of the Cu precipitates prepared both in $H_2O$ solvent and in aqueous 40 vol.% acetic acid solvent, together with the calculated results of the Cu oxalate and its analogues, were as followed: Found for the Cu precipitate prepared in $H_2O$ solvent: C, 15.7·H, 0.6 and for the Cu precipitate prepared in aqueous 40 vol.% acetic acid solvent: C, 15.8·H, 0.7. Calculated for Cu oxalate anhydrate: C, 15.84·H, null; for Cu oxalate monohydrate: C, 14.16·H, 1.19; for Cu oxalate half hydrate: C, 14.96·H, 0.63; for $Cu[(OC(=O)C(=O)OH)]$ $[Cu(C_2HO_4)]$: C, 15.74·H, 0.66. As the Cu precipitate was found to contain H atoms based on the elemental analysis, the Cu precipitate was unable to be identified as Cu oxalate anhydrate which has no H atoms. The Cu precipitates prepared in both pure $H_2O$ solvent and aqueous 40 vol.% acetic acid solvent had almost similar C and H values. These observed C, H values are most identical to those of the $Cu[(OC(=O)C(=O)OH)]$ $[Cu(C_2HO_4)]$ having a oxalate moiety (oxalate mono-anion) in which one of the H atoms was removed. The broad IR peak that appeared at around

$3600 \, cm^{-1}$ as previously described (Fig. 4) also supports the presence of the OH group in the oxalate ligand.

### 3.4. Influence of preparation conditions on the Cu precipitate formation

Cupric nitrate, cupric chloride, cupric oxide (CuO), and cuprous oxide ($Cu_2O$) were utilized as the Cu sources, other than Cu acetate, to prepare the Cu precipitate. The Cu precipitate with the XRD main peak at $2\theta =$ around $23°$ was isolated using any of the Cu sources used here. The Cu precipitates isolated using the Cu salts or oxides were also confirmed to include the oxalate moiety from the observation of the FT-IR spectra, just like the one obtained using Cu acetate.

The preparation of the Cu precipitate was attempted at 303 K in $H_2O$ solvent using, instead of ascorbic acid, pyrocatechol or hydroquinone as the reducing reagent under all the same reaction conditions except for the reducing reagent, however, no Cu precipitate was formed which left the Cu species almost homogeneous.

The preparation of the Cu precipitate was attempted at 303 K in $H_2O$ using ascorbic acid as the reducing reagent in a $N_2$ atmosphere in place of the $O_2$ atmosphere in order to investigate the role of gaseous $O_2$. A reddish powder was observed on the bottom of the reactor in place of the Cu precipitate. The XRD pattern of the reddish powder obtained in the $N_2$ atmosphere was identical to that of the authentic Cu powder (figure not shown). The formation of the Cu precipitate with the oxalate moiety was found to require both ascorbic acid and $O_2$.

The influence of the Cu acetate/ascorbic acid mole ratio on the formation of the Cu precipitate with the oxalate moiety was investigated with a constant amount of ascorbic acid. The XRD pattern of the Cu precipitate obtained for the prescribed mole ratio is illustrated in Fig. 5. The XRD patterns (Fig. 5 (c), (d)) of the Cu precipitates obtained at the Cu acetate/ascorbic acid mole ratios of 1.5 and 2 were in accordance with that of authentic $Cu_2O$. The Cu precipitates obtained at the ratios of 0.5 and 1 were identified as being the Cu precipitate possessing an oxalate moiety based on the observed XRD patterns (Fig. 5 (a), (b)) the main peak being observed at $2\theta =$ around $23°$. The IR spectra of the Cu precipitates obtained at both the Cu acetate/ascorbic acid mole ratios of 0.5 and 1 were also found to have IR peaks based on the oxalate moiety. Thus the formation of the Cu precipitate having an oxalate moiety substantially requires more than an equimolar amount of ascorbic acid for the Cu species.

### 3.5. Time dependence of the formation of the Cu precipitate

The formation of the Cu precipitate was observed with the reaction time at the ascorbic acid/Cu mole ratio of 0.5. The Cu precipitate was isolated at a specific reaction time, and both the XRD pattern (Fig. 6) and the IR spectrum (Fig. 7) of the isolated Cu precipitate were measured. The Cu precipitate isolated immediately after the reaction of the Cu acetate with ascorbic acid in the presence of $O_2$ was identified to be $Cu_2O$ based on the XRD pattern (Fig. 6, 0 h). Thus the $Cu^{2+}$ species is thought to be instantly reduced to $Cu^{1+}$ species by the excess ascorbic acid. With further processing of the reaction time (6 h), the $Cu_2O$ produced during the initial stage was reduced to Cu powder, of which the XRD pattern of the Cu precipitate isolated at 6 h (Fig. 6, 6 h) was quite identical to an authentic Cu powder. The $Cu_2O$ produced immediately after the reaction was thus found to be once more reduced to $Cu^0$ species by the reducing reagent, ascorbic acid, in the reaction system. The XRD pattern of the Cu precipitate isolated after 12 h demonstrated a small but clear XRD peak at $2\theta =$ around $23°$, in addition to the XRD peaks based on the Cu powder. From the reaction times of 12–20 h, the intensities of the XRD peaks due to the Cu powder relative to the intensity of the XRD peak at $2\theta =$ around $23°$ tended to decrease with the reaction time. After 22 h, only the Cu precipitate having an oxalate moiety was isolated as seen in Fig. 6. Thus the Cu precipitate with the oxalate moiety was confirmed to be produced via the $Cu^0$ species. The IR spec-
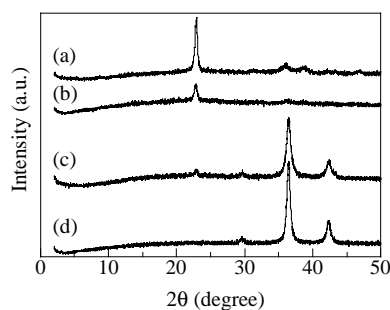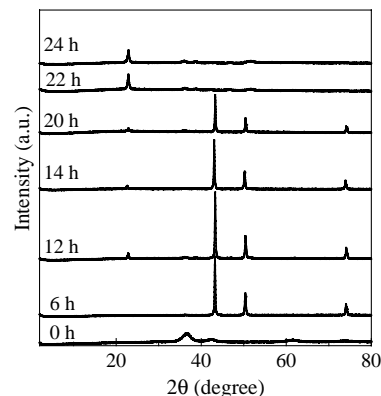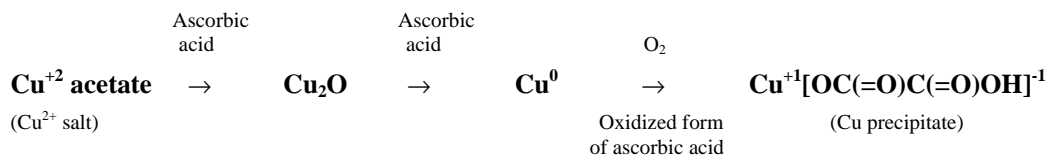


Fig. 5. XRD patterns of the Cu precipitates prepared with different Cu/ascorbic acid mole ratios. Preparation conditions of the Cu precipitate: Cu salt, Cu acetate; solvent, $20 \, cm^3$ of $H_2O$; $O_2$, 0.1 MPa; ascorbic acid, 4 mmol; reaction time, 24 h; reaction temperature, 303 K: (a) Cu/ascorbic acid mole ratio = 0.5; (b) Cu/ascorbic acid mole ratio = 1; (c) Cu/ascorbic acid mole ratio = 1.5; (d) Cu/ascorbic acid mole ratio = 2.



Fig. 6. Variation in XRD patterns of the isolated Cu vs. the reaction time. Preparation conditions: Cu acetate, 2 mmol; solvent, $40 \, cm^3$ of $H_2O$; $O_2$, 0.1 MPa; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 0 (immediately after the reaction), 6, 12, 14, 20, 22, and 24 h.

$$\text{Cu}^{+2} \text{ acetate} \xrightarrow[\text{acid}]{\text{Ascorbic}} \text{Cu}_2\text{O} \xrightarrow[\text{acid}]{\text{Ascorbic}} \text{Cu}^0 \xrightarrow{\text{O}_2} \text{Cu}^{+1}[\text{OC}(=\text{O})\text{C}(=\text{O})\text{OH}]^{-1}$$

(Cu$^{2+}$ salt)                    Oxidized form        (Cu precipitate)
                                   of ascorbic acid

Scheme 1.

tra of the Cu precipitate isolated at the prescribed reaction time also supported the XRD results, thus the IR peaks based on the oxalate moiety were observed in the Cu precipitate sample isolated at the reaction time of 12 h and the intensities of the IR peaks tended to increase with an increase in the reaction time (Fig. 7). The scheme for the formation of the Cu precipitate having an oxalate moiety is as follows (Scheme 1). Cu acetate is first rapidly reduced to $Cu_2O$ by ascorbic acid. The produced $Cu_2O$ is then gradually reduced to $Cu^0$ (Cu powder). With the further reaction time, during which time the ascorbic acid will be almost converted to the corresponding oxidized form, the reduced $Cu^0$ species are once again oxidized to the Cu precipitate with the oxalate moiety (Cu[OC(=O)C(=O)OH]) under the presence of $O_2$. The Cu species of the Cu precipitate will be present as $Cu^{1+}$ because the oxalate mono-anion as a ligand is preferred from the elementary analysis previously described. The decomposition of the oxidized form of ascorbic acid produced during the reduction of $Cu^{2+}$ to $Cu^{1+}$ and $Cu^{1+}$ to $Cu^0$ is thought to participate in the formation of the oxalate moiety, though we have no idea on the definite scheme for the generation of oxalic acid and/or oxalate mono-anion ligand at the present time. The presence of $O_2$ is thought to be necessary to re-oxidize the $Cu^0$ to $Cu^{1+}$. The transformation of the oxidized form of ascorbic acid to oxalic acid (and/or its mono-anion)
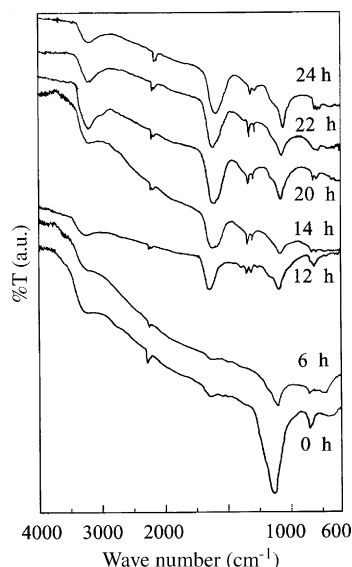
may need $O_2$ if the conversion proceeds through an oxidative decomposition. The deactivation of the Cu catalyst during the liquid-phase oxidation of benzene will be due to the irreversible formation of this Cu ($Cu^{1+}$) precipitate with no regeneration of the active $Cu^{2+}$ species which are responsible for the phenol formation.

## 4. Conclusions

To investigate the Cu precipitate closely correlated with the deactivation of the supported Cu catalyst during the oxidation of benzene to phenol in the presence of both ascorbic acid and gaseous $O_2$, the structure and composition of the Cu precipitate produced during the benzene oxidation were investigated using the Cu precipitate isolated during the reaction of Cu acetate and ascorbic acid in the presence of $O_2$, of which the Cu precipitate had the same XRD pattern as that of the precipitate produced during the benzene oxidation. The XRD pattern of the isolated Cu precipitate was substantially identical to that of the copper oxalate. The elementary analyses of the Cu precipitate suggested that the molecular form is $Cu(C_2HO_4)$. The IR spectra of the Cu precipitate showed peaks based on the oxalate moiety. From these results, the Cu precipitate was identified as the Cu species having an oxalate mono-anion ($Cu^{1+}[OC(=O)C(=O)OH]^{1-}$). From the variation in the XRD pattern of the isolated Cu species versus the reaction time, a scheme for the formation of the $Cu^{1+}[OC(=O)C(=O)OH]^{1-}$ was proposed, in which both $Cu_2O$ and $Cu^0$ are consecutively formed.



Fig. 7. Variation in IR spectra of the isolated Cu vs. the reaction time. Preparation conditions: Cu acetate, 2 mmol; solvent, 40 cm$^3$ of $H_2O$; $O_2$, 0.1 MPa; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 0 (immediately after the reaction), 6, 12, 14, 20, 22, and 24 h.

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