

Liquid-phase oxidation of benzene to phenol by CuO–Al₂O₃ catalysts prepared by co-precipitation method

Takahiro Miyahara^a, Hiroshi Kanzaki^a, Rei Hamada^b, Satoshi Kuroiwa^a,
Satoru Nishiyama^a, Shigeru Tsuruya^{a,*}

^a Faculty of Engineering, Department of Chemical Science and Engineering,
Kobe University, Nada, Kobe 657-8501, Japan

^b Division of Molecular Science, Graduate School of Science and Technology,
Kobe University, Nada, Kobe 657-8501, Japan

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Abstract

The liquid-phase catalytic oxidation of benzene to directly produce phenol was attempted under mild reaction conditions using supported Cu catalysts in aqueous acetic acid solvent. Gaseous oxygen and ascorbic acid were used as an oxidant and a reductant, respectively. Among the supported Cu catalysts studied, the Cu catalysts prepared by the impregnation method, irrespective of the oxide supports, the Cu species were considerably leached during the benzene oxidation. A supported Cu catalyst (CuO–Al₂O₃) prepared by co-precipitation of Cu(NO₃)₂·3H₂O and Al(NO₃)₃·9H₂O inhibited the leaching of Cu species in comparison with the Cu catalysts supported by the impregnation method on Al₂O₃, SiO₂, MCM-41, etc. The influences of the amount of supported Cu, the partial pressure of O₂, the amount of ascorbic acid, the concentration of acetic acid in the solvent, and the reaction temperature on the phenol yield were investigated using the CuO–Al₂O₃ catalyst. The aqueous solvent including high concentration of acetic acid (around 80 vol.%) dramatically inhibited the leaching of Cu species in the CuO–Al₂O₃ catalyst. H₂O₂, which is considered to play an important role in phenol formation, was detected during the benzene oxidation catalyzed by CuO–Al₂O₃. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phenol, one of the important chemical intermediates in the broad industrial fields, has been mainly manufactured using the cumene method by which the selectivity for the phenol is high. However, this cumene process consists of three steps and produces acetone as a byproduct. The one-step production of phenol by direct insertion of oxygen into the benzene ring is an

attractive and challenging method, not only from a practical point of view but also from a synthetic chemical point of view, because the direct oxygenation of the energetically stable benzene to produce phenol has been one of the most difficult oxidation reactions. The gas-phase oxidations of benzene to phenol by nitrous oxide have been studied over H–Ga–ZSM-5 zeolite [1] and in the presence of HZSM-5 [2], in which the influence and the role of Brønsted acidic centers on the activity of phenol formation were discussed. The catalytic hydroxylation of phenol to hydroquinone and catechol over vanadium silicate molecular sieves with

* Corresponding author. Fax: +81-78-8031150.
E-mail address: tsuruya@cx.kobe-u.ac.jp (S. Tsuruya).

MEL structure (VS-2) has been reported in the presence of hydrogen peroxide [3]. Vanadium-exchanged Keggin heteropolyacid (α -1,2-PW₁₀V₂) was reported [4] to be a catalytic precursor of the benzene hydroxylation in the presence of hydrogen peroxide. The catalytic properties of heteropoly complexes containing Fe(III) ions in benzene oxidation has been reported using hydrogen peroxide as an oxidant [5]. Phenol synthesis by liquid-phase oxidation of benzene with molecular oxygen has been studied using iron-heteropoly acid [6] and palladium-heteropoly acid catalytic systems [7], separately. We have also been studying the liquid-phase oxidation of benzene to phenol catalyzed by the Cu catalysts supported on zeolites [8,9] and MCM-41 [10] using molecular oxygen as an oxidant and ascorbic acid as a reductant. We more recently, reported that the liquid-phase oxidation of benzene over supported vanadium catalysts using molecular oxygen and ascorbic acid as oxidant and reductant, respectively [11].

This paper reports the catalytic behavior of the supported Cu catalysts (CuO–Al₂O₃) prepared by co-precipitation of both Cu and Al salts in the liquid-phase oxidation of benzene to phenol. The conditions required to inhibit the leaching of Cu species from the supported Cu catalysts during the benzene oxidation were also investigated in the aqueous acetic acid solvent.

2. Experimental

2.1. Preparation of catalysts

Into the aqueous solution which homogeneously dissolved the prescribed amounts of both Cu(NO₃)₂·3H₂O (Nacalai Tesque, guaranteed reagent) and Al(NO₃)₃·9H₂O (Nacalai Tesque, guaranteed reagent), an aqueous solution of Na₂CO₃ was added dropwise with stirring. After the solution turned alkaline by adding the aqueous Na₂CO₃ solution, the entire solution was stirred at 353 K for 3 h. The resulting precipitate was filtered off under vacuum, washed with ionized water until the filtrate became neutral, dried at 393 K overnight, and calcined at 623 K for 3 h under air (CuO–Al₂O₃ prepared by a co-precipitation method). The amount of Cu content in the CuO–Al₂O₃ catalyst used in this study was usually 1.5 or 3.0 wt. %.

The XRD peaks of CuO (2 0 0), CuO (1 1 2), and CuO (2 0 2) were observed from the XRD measurement of the CuO–Al₂O₃ catalyst. Co-precipitated CuO–SiO₂ and CuO–SiO₂–Al₂O₃ were prepared by a method similar to that of the co-precipitated CuO–Al₂O₃ using Si(OC₂H₅)₄ (Nacalai Tesque, guaranteed reagent) as a Si source. The Cu catalysts impregnated on SiO₂ (JRC-SiO-8), Al₂O₃ (JRC-ALO-4), SiO₂–Al₂O₃ (JRC-SAL-2), MCM-41 (prepared according to Ref. [9]), and HMCM-41 (prepared according to Ref. [10]) were prepared by a conventional impregnation method using Cu(CH₃COO)₂·H₂O in ethanol solvent as a Cu source. All the supported Cu catalysts prepared by the impregnation method were dried at 393 K overnight and calcined at 773 K for 5 h in air flow. The Cu ion-exchanged catalysts were prepared by a conventional ion-exchange method using NaY (Toso, Si/Al atomic ratio = 2.8) and HMCM-41 (Si/Al atomic ratio = 55) as a support. The Cu-supported catalysts prepared by the ion-exchange method were washed with deionized water, dried at 393 K overnight, and calcined at 773 K for 5 h in air. The Cu amounts supported on the various oxides were determined by an atomic absorption spectrometer (Shimadzu type AA-630-01) after the catalysts were homogeneously dissolved by adding a few drops of hydrofluoric acid.

2.2. Liquid-phase oxidation of benzene

Benzene (Nacalai Tesque, guaranteed reagent) and ascorbic acid (Nacalai Tesque, guaranteed reagent) were used without further purification. A typical oxidation procedure is as follows: 2 cm³ of benzene (22.5 mmol), 0.4 g of CuO–Al₂O₃, and L-ascorbic acid (4 mmol) were added to 20 cm³ of aqueous acetic acid solvent (5.7 vol. % (1 mol/l)). The benzene oxidation was performed using a magnetic stirrer at 303 K in oxygen atmosphere (1 atm). After propane-2-ol, as an internal standard, was added to the reaction solution and the solid catalyst was separated by centrifugation, the products were analyzed at 453 K by a Shimadzu GLC with an FID (Type GC-8A) using a 3 m stainless column packed with Silicon OV-17. Propane-2-ol was confirmed to be not oxidized to acetone during this treatment. The catalytic activity for phenol formation was usually compared at reaction time of 5 or 24 h. The Cu amount leached into the reaction solution

during the benzene oxidation was analyzed by atomic absorption measurement (Shimadzu type AA-630-01).

2.3. Quantitative measurement of hydrogen peroxide (H_2O_2)

The amount of hydrogen peroxide accumulated during the benzene oxidation was quantitatively measured by iodometry [12]. The homogeneous reaction solution separated from the solid catalyst by centrifugation, to which small amounts of sodium hydrogen carbonate were added to prevent the autoxidation of I^- ions, was quickly analyzed in a dark atmosphere.

2.4. Quantitative measurement of surface Cu species by N_2O titration

The surface Cu species of the $CuO-Al_2O_3$ catalyst were quantitatively measured by N_2O titration method ($2Cu + N_2O \rightarrow Cu_2O + N_2$) using a fixed-bed flow reaction system. A 0.1 g of the $CuO-Al_2O_3$ catalyst (150–250 μm) placed into the reactor was reduced at 623 K for 2 h under H_2 flow, followed by maintaining the same temperature for 1 h under He flow to remove the adsorbed H_2 . N_2O was introduced at 0.25 cm^3 per pulse until no N_2 was detected. The gas analyses were conducted using a GLC (Shimadzu type GC-4A; detector, TCD) with a 0.5 m stainless steel column (i.d. 3 mm) containing Unibeads C at 474 K under a He carrier.

3. Results and discussion

3.1. Effects of catalyst support and support method on the liquid-phase oxidation of benzene to phenol

The present reaction system is a slurry in which the two liquid phases, benzene and water, include. The effect of the various mass transfer limitations will be, however, not so important because of the considerable low rate of the phenol production in the present reaction condition. The catalytic activity of the catalyst was, thereafter, compared as a yield of phenol produced under stirring at a prescribed reaction time. The state of the active Cu species, thus heterogeneous and/or homogeneous Cu species, for the phenol formation depended on both the catalyst prepared and the solvent utilized. The active Cu species of a catalytic system in a prescribed solvent are suggested below, based on the data of the Cu leaching. No other products such as hydroquinone and/or catechol were detected in the reaction conditions carried out in this study.

The influences of the support and the support method of supported Cu catalysts on the phenol yield and the Cu leaching in 5.7 vol.% (1 mol/l) acetic acid aqueous solvent were recorded in Table 1. Only phenol was detected under the present reaction conditions using the Cu catalysts as shown in Table 1. The Cu-impregnated catalysts studied here gave 0.7–1.0% phenol yields. The amounts of Cu leaching from these Cu-impregnated catalysts during the benzene

Table 1
Liquid-phase benzene oxidation over Cu catalysts supported on various oxide supports^a

| Catalyst | Cu (wt.%) | Si/Al ratio | Phenol yield (%) | Cu leaching (%) |
|--|-----------|-------------|------------------|-----------------|
| Cu/SiO ₂ ^b | 1.0 | – | 0.7 | 82 |
| Cu/Al ₂ O ₃ ^b | 1.0 | – | 0.9 | 90 |
| Cu/SiO ₂ -Al ₂ O ₃ ^b | 1.0 | 43 | 1.0 | ^c |
| Cu/MCM-41 ^b | 1.1 | – | 0.9 | 94 |
| Cu/HMCM-41 ^b | 1.0 | 55 | 1.0 | 65 |
| Cu-HMCM-41 ^d | 1.0 | 55 | 1.1 | 92 |
| Cu-NaY ^d | 2.0 | 2.8 | 0.7 | 90 |
| CuO-SiO ₂ ^e | 3.0 | – | 0.1 | 8.5 |
| CuO-Al ₂ O ₃ ^e | 3.0 | – | 0.9 | 9.0 |

^a Catalyst, 0.4 g; benzene, 2 cm^3 (22.5 mmol); solvent, 20 cm^3 of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 5 h.

^b Impregnation method.

^c Not measured.

^d Ion-exchange method.

^e Co-precipitation method.

Table 2

Liquid-phase benzene oxidation by CuO–Al₂O₃ and Cu(CH₃COO)₂ catalysts in aqueous acetic acid solvent^a

| Catalyst | Phenol yield (%) | Phenol/Cu (ratio) |
|--------------------------------------|------------------|------------------------|
| Cu(CH ₃ COO) ₂ | 1.1 | 1.3 |
| CuO–Al ₂ O ₃ | 0.9 | 1.1 (4.0) ^b |

^a Cu(CH₃COO)₂, 0.189 mmol; catalyst, 0.4 g of CuO–Al₂O₃ (Cu, 3 wt.%); benzene, 2 cm³ (22.5 mmol); solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solvent; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 5 h.

^b Surface Cu species (0.051 mmol) measured by N₂O titration (see Section 2) were used to calculate the phenol/Cu ratio.

oxidation were 65–94%. The Cu ion-exchanged HMCM-41 and NaY catalysts also gave 0.7–1.1% phenol yields, and the percentages of Cu leaching of both catalysts reached 90–92%. The Cu species leached in the reaction solution will thus mainly participate in the phenol formation in the case of the Cu catalysts ion-exchanged or impregnated on various oxide in 5.7 vol.% acetic acid aqueous solvent, taking into account of the results of Table 2, in which unsupported Cu species were found to have catalytic activity for phenol formation.

The leaching of the Cu species from the supported Cu catalysts during the benzene oxidation was appreciably inhibited by the Cu-supported catalysts prepared by the co-precipitation method. Thus, the percentages of Cu leaching of both CuO–SiO₂ and CuO–Al₂O₃, which were prepared by co-precipitation, were 8.5 and 9.0, respectively. The heterogeneous Cu species on the CuO–Al₂O₃ (or CuO–SiO₂) catalysts in 5.7 vol.% acetic acid aqueous solvent will mostly function as the catalytic active species for phenol formation, although the role of the Cu species leached in the reaction solution cannot ignore. The co-precipitated CuO–Al₂O₃ is hereafter studied as a catalyst for liquid-phase oxidation of benzene, because the CuO–Al₂O₃ gave a phenol yield of 0.9%, and the percentage of Cu leaching was considerably lower than the Cu-supported catalysts prepared by both impregnation and ion-exchange methods.

A comparison in the turnover number (the produced phenol/Cu ratio) between the heterogeneous CuO–Al₂O₃ and the unsupported Cu(CH₃COO)₂ catalysts was attempted in aqueous acetic acid (5.7 vol.% (1 mol/l)) solvent (Table 2). Both the unsupported Cu(CH₃COO)₂ and the heterogeneous CuO–Al₂O₃

Table 3

Liquid-phase benzene oxidation by CuO–Al₂O₃ catalysts in aqueous solvent^a

| Solvent | Phenol yield (%) | Cu leaching (%) |
|---|------------------|-----------------|
| H ₂ O | 0.45 | 8.8 |
| Aqueous CH ₃ OH (1 mol/l) | 0.26 | 6.1 |
| Aqueous C ₂ H ₅ OH (1 mol/l) | 0.22 | 6.7 |
| Aqueous (CH ₃) ₂ COH (1 mol/l) | 0.27 | 7.7 |
| Aqueous (COOH) ₂ (1 mol/l) | 0.06 | 0.35 |
| Aqueous CH ₃ COOH (1 mol/l) | 0.90 | 9.0 |

^a Catalyst, 0.4 g of CuO–Al₂O₃ (Cu, 3 wt.%); benzene, 2 cm³ (22.5 mmol); solvent, 20 cm³; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 5 h.

have almost similar turnover numbers. The turnover number of the CuO–Al₂O₃ catalyst calculated using the surface Cu species obtained by a N₂O titration measurement was considerably greater, although the reduced Cu surface area may be different from the original one because of the reduction treatment. The surface Cu species on the CuO–Al₂O₃ catalyst will be effectively utilized for the formation of phenol.

3.2. Liquid-phase oxidation of benzene catalyzed by co-precipitated CuO–Al₂O₃

The liquid-phase benzene oxidation by the CuO–Al₂O₃ catalyst was attempted using various aqueous solvents (Table 3). The percentage of the Cu leaching in each solvent during the benzene oxidation was also measured. Phenol was produced even in pure H₂O solvent. The aqueous solvents containing alcohol or oxalic acid rather inhibited the formation of phenol. As the aqueous solvent containing acetic acid was the best one for producing phenol among the aqueous solvents studied here, aqueous acetic acid solvent will be hereafter utilized as a solvent for the benzene oxidation.

Fig. 1 illustrates the dependence of the phenol yield on the reaction time using the reaction temperature of 303 K. The yield of phenol almost linearly increased with the increase in the reaction time up to around 5 h, but the degree of the increase in the phenol yield sharply declined at the reaction times of more than 10 h. Thus, the deactivation of the CuO–Al₂O₃ catalyst proceeded with benzene conversion to phenol. We have attempted a benzene oxidation using a used

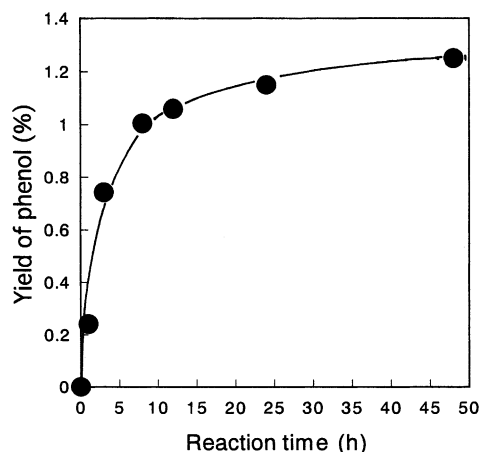


Fig. 1. Dependence of the yield of phenol on reaction time. Benzene, 2 cm³ (22.5 mmol); catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; ascorbic acid, 4 mmol; O₂ pressure, 1 atm; reaction temperature, 303 K.

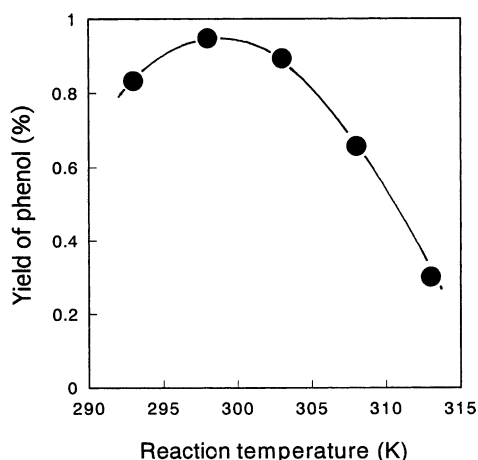


Fig. 2. Dependence of the yield of phenol on reaction temperature. Benzene, 2 cm³ (22.5 mmol); catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; ascorbic acid, 4 mmol; O₂ pressure, 1 atm; reaction time, 5 h.

Cu-supported Al₂O₃ (Cu/Al₂O₃) catalyst which was washed with acetone, dried overnight, and calcined at 775 K for 5 h in air flow. The initial activity for phenol formation was almost recovered using the used catalyst. The results suggest that the deactivation of the supported Cu catalyst will be mainly due to blocking of the active Cu site on the catalyst by phenol produced and/or its oxidation products.

The dependence of the yield of phenol on the reaction temperature is shown in Fig. 2. The yield of phenol passed through a maximum value at a temperature around 298 K, and a further increase in the reaction temperature inversely caused a decrease in the yield of phenol. A similar behavior of the phenol yield by the variation of the reaction temperature has been observed using both Cu–NaY [8,9] and Cu/MCM-41 [10] catalysts. One of the reasons for the decline in the phenol yield at higher reaction temperatures is considered to be a decrease in the solubility of oxygen molecules in the aqueous solvent at higher temperatures. At higher reaction temperature, the self-oxidation of ascorbic acid itself added as a reductant will also cause a decrease in the phenol yield.

The dependence of the phenol yield on the partial pressure of O₂ was investigated at the reaction temperature of 303 K (Fig. 3). The yield of phenol

increased with an increase in the partial pressure of O₂ up to pressures of around 1 atm. Further increase in the partial pressure of O₂ caused no increase in the phenol yield and kept the phenol yield almost constant. Both Cu/SiO₂ and Cu/NaY catalysts prepared by an impregnation method have also been reported

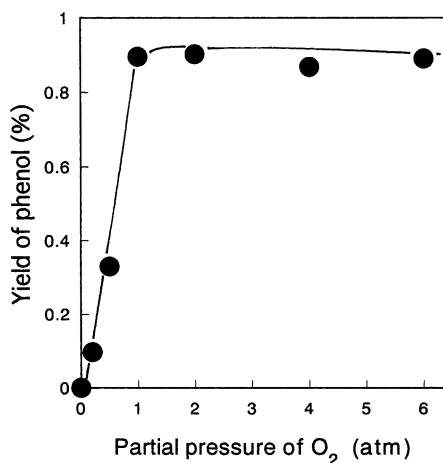


Fig. 3. Dependence of the yield of phenol on the partial pressure of O₂. Benzene, 2 cm³ (22.5 mmol); catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 5 h.

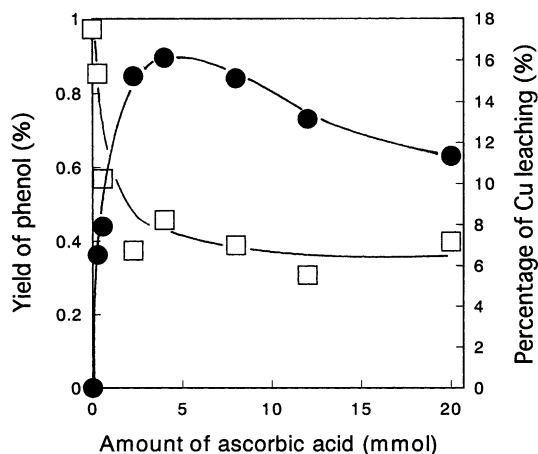


Fig. 4. Influence of the amount of ascorbic acid on the yield of phenol and the percentage of Cu leaching. Benzene, 2 cm³ (22.5 mmol); catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; reaction temperature, 303 K; reaction time, 5 h. (●) Yield of phenol; (□), percentage of Cu leaching.

[11] for the phenol yield to behave almost similarly under the O₂ pressures of 1 and 4 atm.

The influence of the amount of ascorbic acid on the phenol yield is illustrated in Fig. 4. No phenol was produced in the absence of ascorbic acid. The yield of phenol increased with the increase in the amount of ascorbic acid up to about 4 mmol, but further addition of ascorbic acid caused a decrease in the yield of phenol. Too much ascorbic acid, which functions as a reductant, will lead to the reductive decomposition of hydrogen peroxide which is produced during the benzene oxidation and plays an important role in phenol formation, as described later.

The dependence of the phenol yield on the fraction of acetic acid in the aqueous solvent is illustrated in Fig. 5. The percentage of the Cu leaching was also measured and plotted in Fig. 5. Phenol was produced even in the absence of acetic acid although the yield was not high. The yield of phenol passed through a maximum value at the fraction of acetic acid of around 40–50 vol.%. Further increase in the fraction of acetic acid inversely caused the decrease in the phenol yield. Only a small amount of phenol was obtained in 100 vol.% acetic acid solvent. The percentage of the Cu leaching increased with the increase in the percentage of the fraction of acetic acid up to the fractions of 40–50 vol.% in a manner similar to the

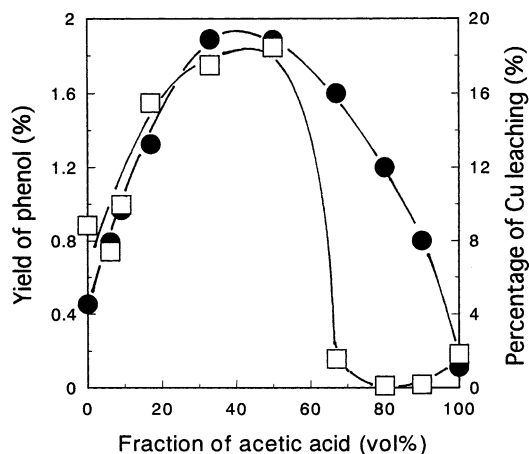


Fig. 5. Influence of the fraction of acetic acid on the yield of phenol and the percentage of Cu leaching. Benzene, 2 cm³ (22.5 mmol); catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; ascorbic acid, 4 mmol; solvent, 20 cm³ of acetic acid aqueous solution; reaction temperature, 303 K; reaction time, 5 h. (●) Yield of phenol; (□), percentage of Cu leaching.

yield of phenol. However, the percentage of the Cu leaching abruptly declined at fractions of acetic acid more than around 50 vol.% as illustrated in Fig. 5, and the leaching of Cu species from the co-precipitated CuO–Al₂O₃ catalyst was inhibited up to almost zero. The degree of decrease in the Cu leaching was greater than that of the yield of phenol. Thus, aqueous solvent consisting of an acetic acid fraction of around 65–80 vol.% has been found to have both advantages: to almost inhibit the Cu leaching, and also to give a near-maximum yield of phenol. The benzene oxidation in the 80 vol.% acetic acid aqueous solvent using CuO–Al₂O₃ catalyst gave the phenol yield of 1.2% with the only 0.1% Cu leaching. The active Cu species of the CuO–Al₂O₃ catalyst in 80 vol.% acetic acid aqueous solvent are thus heterogeneous Cu ones supported on the CuO–Al₂O₃ catalysts.

The benzene oxidation in 80 vol.% acetic acid aqueous solvent was attempted using various supported Cu catalysts to investigate the effect of a higher concentration of acetic acid on the Cu leaching during the oxidation (Table 4). A comparison of the Cu leaching during the benzene oxidation in the aqueous solvents of both 5.7 vol.% (Table 1) and 80 vol.% (Table 4) acetic acid indicates that the 80 vol.% acetic acid aqueous solvent dramatically inhibited the Cu leaching during the benzene oxidation. Furthermore, the yield of phenol

Table 4
Liquid-phase benzene oxidation over supported Cu catalysts in aqueous 80 vol.% acetic acid solvent^a

| Catalyst | Cu (wt.%) | Phenol yield (%) | Cu leaching (%) |
|---|-----------|------------------|-----------------|
| CuO–Al ₂ O ₃ ^b | 3.0 | 1.2 | 0.1 |
| CuO–SiO ₂ –Al ₂ O ₃ ^b | 3.0 | 1.6 | 0.8 |
| Cu/SiO ₂ ^c | 1.0 | 0.9 | 3.6 |
| Cu–HMCM-41 ^d | 0.94 | 2.2 | 3.9 |

^a Catalyst, 0.4 g; benzene, 2 cm³ (22.5 mmol); solvent, 20 cm³ of 80 vol.% acetic acid aqueous solution; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 5 h.

^b Co-precipitation method.

^c Impregnation method.

^d Ion-exchange method.

(Table 4) obtained in 80 vol.% acetic acid aqueous solvent was greater than that (Table 1) in 5.7 vol.% acetic acid aqueous solvent, irrespective of the supported Cu catalysts. Although we have yet no experimental evidence for interpreting the specific behavior of aqueous high acetic acid solvent inhibiting the Cu leaching, the high concentration of acetic acid in the aqueous acetic acid solvent was thus found to be a favorable solvent because of the effective inhibiting effect of the Cu leaching, in addition to a higher catalytic activity for phenol production. MCM-41 was an attractive support for phenol production among the supports used in this study, because the Cu ion-exchanged MCM-41 catalyst (Cu–HMCM-41) in the high acetic acid gave almost two times higher activity for phenol formation, keeping the low percentage of the Cu leaching, than the CuO–Al₂O₃ catalyst (Table 4).

The oxidation of benzene catalyzed by the CuO–Al₂O₃ was attempted using reductants other than ascorbic acid to investigate the effect of a reductant on phenol production (Table 5). Hydroquinone and pyrocatechol were effective for phenol production, although the phenol yield was lower than when ascorbic acid was utilized. Only a trace of phenol was formed using zinc species.

3.3. H₂O₂ accumulated during benzene oxidation catalyzed by CuO–Al₂O₃ and benzene oxidation using H₂O₂ as an oxidant

The H₂O₂ accumulated during the benzene oxidation using the CuO–Al₂O₃ catalyst in the presence of

Table 5
Liquid-phase benzene oxidation over CuO–Al₂O₃ catalyst using various reductants^a

| Reducing agent | Phenol yield (%) |
|------------------|------------------|
| Ascorbic acid | 1.3 |
| Hydroquinone | 0.5 |
| Pyrocatechol | 0.5 |
| Zinc powder | Trace |
| Zinc acetate | Trace |
| Sodium sulfite | Trace |
| Oxalic acid | 0 |
| Isobutyraldehyde | 0 |

^a Catalyst, CuO–Al₂O₃ (Cu, 1.5 wt.%), 0.4 g; benzene, 2 cm³ (22.5 mmol); solvent, 20 cm³ of 80 vol.% acetic acid aqueous solution; reducing agent, 4 mmol; reaction temperature, 303 K; reaction time, 24 h; pressure, 1 atm of O₂.

both oxygen as an oxidant and ascorbic acid as a reductant was quantitatively measured by an idometric method (Fig. 6). The accumulated amount of H₂O₂ almost linearly increased with an increase in the reaction time up to around 5 h. However, further increase in the reaction time inversely caused a decrease in the amount of H₂O₂; thus, the amount of H₂O₂ passed through a maximum value at the reaction time of around 5 h. The yield of phenol increased with the reaction time in a similar manner as the accumulated

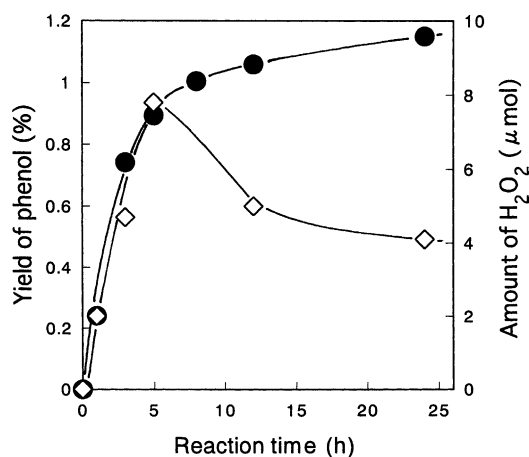


Fig. 6. Plots of the yield of phenol and accumulated H₂O₂ amount vs. reaction time. Benzene, 2 cm³ (22.5 mmol); catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; ascorbic acid, 4 mmol; solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; reaction temperature, 303 K; reaction time, 5 h. (●) Yield of phenol; (□), amount of H₂O₂.

Table 6
Influences of ascorbic acid and molecular oxygen on formations of both H₂O₂ and phenol^a

| Run | Ascorbic acid (mmol) | O ₂ | H ₂ O ₂ (μmol) | Phenol (%) |
|-----|----------------------|----------------------|--------------------------------------|------------|
| 1 | 4 | Absent | 0 | 0 |
| 2 | 0 | Present ^b | 0 | 0 |
| 3 | 4 | Present ^b | 7 | 0.9 |

^a Catalyst, CuO–Al₂O₃ (Cu, 3 wt.%), 0.4 g; benzene, 2 cm³ (22.5 mmol); solvent, 20 cm³ of 5.7 vol.% (1 mol/l) acetic acid aqueous solution; reaction temperature, 303 K; reaction time, 5 h.

^b Pressure, 1 atm.

amount of H₂O₂ in the initial stage of the benzene oxidation, as illustrated in Fig. 6. The decline in the accumulated amount of H₂O₂ after the reaction time of ca. 5 h may be in part caused by self-decomposition of H₂O₂ and/or the deactivation of the CuO–Al₂O₃ catalyst. Table 6 shows the influences of ascorbic acid and oxygen on both the formations of H₂O₂ and phenol. The presence of both O₂ and ascorbic acid were confirmed to be necessary for the formation of H₂O₂ in the presence of the CuO–Al₂O₃ (Cu, 3.0 wt.%) catalyst. The production of phenol catalyzed by CuO–Al₂O₃ in the presence of both O₂ and ascorbic acid will be closely related to the formation of H₂O₂, as evidenced from the results of Fig. 6 and Table 6.

The oxidation of benzene by CuO–Al₂O₃ (Cu, 1.5 wt.%) catalyst was attempted under various reaction conditions using H₂O₂ as an oxidant, instead of O₂ (Table 7). When H₂O₂ was not present, no phenol was produced in the absence of either ascorbic acid or O₂ (Table 7, Runs 1, 2). Phenol was obtained in a 1.6% yield when H₂O₂ was used as an oxidant in the presence of both ascorbic acid and O₂. However, it is of interest to note that the CuO–Al₂O₃

catalyst–ascorbic acid–O₂ system gave a comparable yield (1.3%) of phenol even without H₂O₂ (Table 7, Run 3). Also, it was found that H₂O₂ as an oxidant could not be effectively utilized for phenol production when no O₂ or ascorbic acid was available (Table 7, Runs 5 and 6). The formation of H₂O₂ was thus confirmed in the presence of O₂, ascorbic acid and CuO–Al₂O₃ catalyst, and the formed H₂O₂ was found to play an important role in phenol production and to effectively function in the formation of phenol in the presence of both ascorbic acid and O₂.

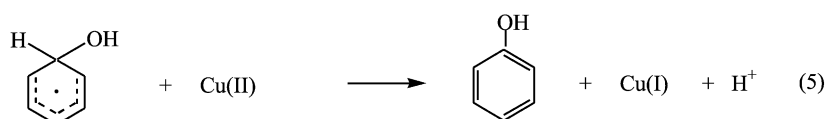
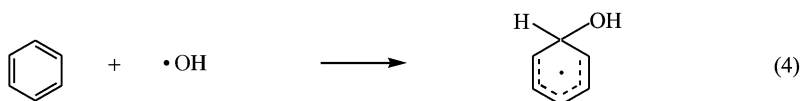
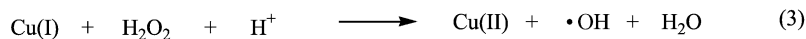
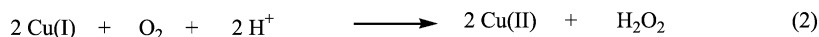
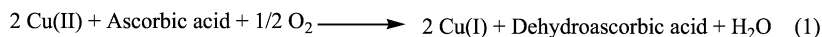
3.4. A plausible Fenton-type scheme for benzene oxidation to phenol catalyzed by CuO–Al₂O₃

As described in the previous section, both oxygen as an oxidant and ascorbic acid as a reductant were necessary for the production of phenol from the benzene oxidation catalyzed by the CuO–Al₂O₃. The catalytic oxidation of ascorbic acid in Cu(II)–ascorbic acid–O₂ system has been kinetically studied in detail and a new type of chain mechanism including CuO₂(I) species was proposed [13]. The formation of H₂O₂ was confirmed in the presence of both O₂ and ascorbic acid, and the amount of accumulated H₂O₂ was closely related to the yield of phenol, particularly during the initial stage of the benzene oxidation. Phenol was yielded in the presence of H₂O₂, instead of both O₂ and ascorbic acid, in the benzene oxidation catalyzed by the CuO–Al₂O₃. However, the H₂O₂ was more effectively utilized for phenol production in the presence of both O₂ and ascorbic acid. Based on these results and the similarity of the CuO–Al₂O₃ catalyst in the presence of both O₂ and ascorbic acid to the Fenton-type reagent [14,15], the following Scheme 1

Table 7
Benzene oxidation catalyzed by CuO–Al₂O₃ using H₂O₂ as an oxidant^a

| Run | H ₂ O ₂ (mmol) | Ascorbic acid (mmol) | Atmosphere | Phenol yield (%) |
|-----|--------------------------------------|----------------------|----------------|------------------|
| 1 | 0 | 0 | O ₂ | 0 |
| 2 | 0 | 4 | N ₂ | 0 |
| 3 | 0 | 4 | O ₂ | 1.3 |
| 4 | 9.6 | 4 | O ₂ | 1.6 |
| 5 | 9.6 | 4 | N ₂ | 0.7 |
| 6 | 9.6 | 0 | O ₂ | 0.2 |

^a Catalyst, CuO–Al₂O₃ (Cu, 1.5 wt.%), 0.4 g; benzene, 2 cm³ (22.5 mmol); solvent, 20 cm³ of 80 vol.% acetic acid aqueous solution; reaction temperature, 303 K; reaction time, 24 h; pressure, 1 atm.



Scheme 1.

is thought to be a plausible one for the benzene oxidation to phenol catalyzed by $\text{CuO-Al}_2\text{O}_3$ in the presence of both O_2 and ascorbic acid. The first step (1) indicates that Cu(II) species (Cu(II) species supported on the catalyst and/or Cu(II) species leached in the reaction solution) are reduced to Cu(I) by ascorbic acid. The resulting Cu(I) causes the O_2 reduction to form hydrogen peroxide in the presence of H^+ (step 2). The hydroxyl radical, generated from the decomposition of the formed H_2O_2 in the presence of Cu(II) species and proton (step 3), will add to benzene to form hydroxycyclohexadienyl radical (step 4). The participation of the hydroxy radical during the benzene oxidation catalyzed by Cu/MCM-41 has been suggested [10] from the retardation effect of the added alcohol. The corresponding radical will produce phenol in the presence of Cu(II) species according to step (5). The participation of the hydroxy radical has been suggested in the benzene oxidation catalyzed by Cu -supported mesoporous silicates from the results that the added alcohol, which acts as scavenger for hydroxy radical, decreased the yield of phenol [10]. The results that the decomposition of H_2O_2 to form a hydroxy radical was promoted by the presence of both O_2 and ascorbic acid (Table 7) support step (3), in which hydrogen peroxide is decomposed in the presence of reduced Cu(I) species. The Cu(I) species will

be formed by the reduction of Cu(II) by the presence of both O_2 and ascorbic acid as shown in step (1).

4. Conclusions

The liquid-phase oxidation of benzene by various supported Cu catalysts was attempted in order to produce phenol directly using molecular oxygen as an oxidant and ascorbic acid as a reductant. Among the supported Cu catalysts studied in this report, the $\text{CuO-Al}_2\text{O}_3$ catalyst prepared by a co-precipitation method was found to be an effective catalyst for phenol production with low Cu leaching. The aqueous solvent containing high percentage (around 80 vol.%) acetic acid was a good solvent for phenol formation and drastically inhibited the Cu leaching from the $\text{CuO-Al}_2\text{O}_3$ catalyst during the benzene oxidation. The high volume percentage acetic acid (80 vol.%) aqueous solvent was also a satisfactory one for the benzene oxidation to produce phenol using the other supported Cu catalysts including Cu-HMCM-41 , with a comparatively high catalytic activity for phenol production and a low Cu leaching. The influence of O_2 partial pressure, amount of ascorbic acid, and reaction temperature on the phenol yield was investigated using the $\text{CuO-Al}_2\text{O}_3$ catalyst. The accumulation of H_2O_2

was confirmed during the benzene oxidation. Phenol was produced using the H_2O_2 oxidant in the presence of the $\text{CuO-Al}_2\text{O}_3$ catalyst. The phenol formation was closely related to the formation of H_2O_2 . Fenton-type reaction scheme including hydrogen peroxide as an intermediate was a plausible one for the benzene oxidation to produce phenol catalyzed by $\text{CuO-Al}_2\text{O}_3$ in the presence of both O_2 and ascorbic acid.

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References

- [1] M. Hafele, A. Reitzmann, D. Roppelt, G. Emig, *Appl. Catal. A* 150 (1997) 153.
- [2] V.I. Sobolev, K.A. Dubkov, E.A. Paukshtis, L.A. Pirutko, M.A. Rodkin, A.S. Kharitonov, G.I. Panov, *Appl. Catal. A* 141 (1996) 185.
- [3] P.R. Hari, A.V. Ramaswamy, *Appl. Catal. A* 93 (1993) 123.
- [4] K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, Y. Shimizu, *J. Mol. Catal.* 114 (1996) 181.
- [5] L.I. Kuznetsova, L.G. Deuusheva, M.A. Fedotov, V.A. Likholobov, *J. Mol. Catal. A* 111 (1996) 81.
- [6] Y.-Y. Seo, Y. Mukai, T. Tagawa, S. Goto, *J. Mol. Catal. A* 120 (1997) 149.
- [7] L.C. Passoni, A.T. Cruz, R. Buffon, U. Schuchardt, *J. Mol. Catal. A* 120 (1997) 117.
- [8] T. Ohtani, S. Nishiyama, S. Tsuruya, M. Masai, in: L. Guzzi, F. Solymosi, P. Tetenyi (Eds.), *Proceedings of the 10th International Congress on Catalysis, Budapest, 1992*, Elsevier, Amsterdam, 1993, p. 1999.
- [9] T. Ohtani, S. Nishiyama, S. Tsuruya, M. Masai, *J. Catal.* 155 (1995) 158.
- [10] J. Okamura, S. Nishiyama, S. Tsuruya, M. Masai, *J. Mol. Catal. A* 135 (1998) 133.
- [11] M. Ishida, Y. Masumoto, R. Hamada, S. Nishiyama, S. Tsuruya, M. Masai, *J. Chem. Soc. Perkin Trans. 2* (1999) 847.
- [12] M. Ishibashi, *Teiryō Bunseki Jikken Shishin* (Experimental Quantitative Analysis), Toyama Shobou, 1965, p. 259.
- [13] E.V. Shtamm, A.P. Purmal, Yu.I. Skurlatov, *Int. J. Chem. Kinet.* XI (1979) 461.
- [14] F. Haber, J. Weiss, *Proc. Roy. Soc. Lond. A* 147 (1934) 332.
- [15] W.T. Dixon, R.C.O. Norman, *J. Chem. Soc.* (1964) 4857.