



Activities for phenol formation using Cu catalysts supported on Al₂O₃ in the liquid-phase oxidation of benzene in aqueous solvent with high acetic acid concentration

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

^a Department of Chemical Science and Engineering, Faculty of 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 oxidation of benzene to phenol using a Cu catalyst supported on Al₂O₃ was studied at 303 K in an aqueous solvent with a variety of concentrations of acetic acid. Gaseous O₂ and ascorbic acid were utilized as an oxidant and a reducing reagent, respectively. An aqueous solvent with more than around 70–80 vol.% acetic acid concentration was confirmed to cause a sharp apparent decrease in the Cu leaching from a Cu catalyst (Cu/Al₂O₃) impregnated on Al₂O₃, as well as a CuO-Al₂O₃ catalyst prepared by a co-precipitation method reported previously, during the benzene oxidation, keeping the yield of phenol comparatively high. The apparent Cu leaching was largely inhibited in an aqueous solvent with high acetic acid concentration in comparison with a solvent of low acetic acid concentration, irrespective of the presence of benzene and/or ascorbic acid. The influences of both the Cu amount supported on the Cu/Al₂O₃ catalyst and the amount of ascorbic acid on the yield of phenol were investigated in the aqueous solvents with acetic acid concentrations of both 5.7 and 80 vol.%. The Cu/Al₂O₃ catalyst in the aqueous acetic acid solvent was deactivated in the comparatively initial stage of the oxidation of benzene. The catalytic activity of the used Cu supported catalyst for phenol formation was almost completely recovered by calcining the catalyst at 773 K. The amount of the deactivated Cu species based on a XRD peak at $2\theta = 23^\circ$ in the used Cu/Al₂O₃ catalyst was found to have a correlation with the yield of phenol.

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1. Introduction

More than 90% of phenol, one of the important chemicals in the practical fields of resin, fiber, and medicine, has been produced by a cumene method [1,2]. The disadvantage of this method is the inclusion of a three-step process, although the selectivity in the each step is quiet high, and the yield of a by-product, acetone, in addition to phenol formation [3]. Phenol production by the toluene method, which includes a two-step process and produces no by-product such as acetone, has been performed [4] in a few practical chemical plants. A one-step production of phenol through the direct oxygenation of benzene has so far been attempted using various catalytic systems by many researchers. The practical

development of the one-step production of phenol will have advantages in cost reduction and energy saving [3]. Phenol formation via the direct oxygenation of benzene formally includes insertion of an oxygen atom between the C–H bond of benzene. Because of the high stability of benzene, the direct oxygenation of benzene to form phenol has been thought to be one of the most difficult oxidation reactions but also to be one of the most challenging oxidation reactions from the point of view of organic synthetic chemistry. A direct hydroxylation of benzene has been reported using an Fe²⁺-H₂O₂ system (Fenton's reagent) by Norman and co-workers [5]. An Fe³⁺-H₂O₂-catechol system (Hamilton reagent) has also been utilized for the oxygenation of benzene [6]. The oxygenation of benzene using molecular oxygen, which will be less expensive and more easily handled, as an oxidant instead of hydrogen peroxide, has been attempted [7]. More recently, noble metal-vanadium (V) oxide catalysts supported on silica have been reported

* Corresponding author. Tel.: +81-78-8036171; fax: +81-78-8036171.
E-mail address: tsuruya@cx.kobe-u.ac.jp (S. Tsuruya).

to be active for benzene oxidation to phenol in the presence of both gaseous oxygen and hydrogen under a pressurized atmosphere [8,9]. The benzene oxidation to phenol has also been attempted using an $\text{EuCl}_3\text{-TiO}(\text{acac})_2$ catalyst with Zn as a reducing reagent [10] or using a partially exchanged heteropoly acid as a catalyst [11–13]. Phenol formation by the direct hydroxylation of benzene with both oxygen and hydrogen on platinum catalyst supported on SiO_2 has been reported to be accelerated when acetylacetonate of vanadium was added to the reaction medium [14]. The reductive oxidation of benzene to phenol with both O_2 and H_2 has been reported using the catalytic palladium membrane [15,16]. We have reported the liquid-phase oxidation of benzene to phenol catalyzed by Cu catalysts [17–19] supported on various oxides including zeolites, MCM-41 and a $\text{CuO-Al}_2\text{O}_3$ catalyst [20] prepared by a co-precipitation method using gaseous oxygen as an oxidant and ascorbic acid as a reducing reagent. Vanadium catalysts [21,22] supported on SiO_2 and Al_2O_3 , instead of the supported Cu catalysts, have also been utilized for the benzene oxidation using gaseous oxygen as an oxidant and ascorbic acid as a reducing reagent. On the way to conduct our recent study on the liquid-phase benzene oxidation to phenol using the Cu catalysts ($\text{CuO-Al}_2\text{O}_3$) prepared by a co-precipitation method, an aqueous solvent with high acetic acid concentration has been found [20] to have a specific character for apparently inhibiting the apparent Cu leaching from the $\text{CuO-Al}_2\text{O}_3$ catalyst, together with a higher yield of phenol, during the benzene oxidation. Supported V catalysts in the aqueous solvent with high acetic acid were also reported [22] to have high catalytic activity for phenol formation, though the V leaching was not decreased, in the benzene oxidation.

In this study, we have mainly investigated the catalytic behavior of the Cu catalysts impregnated on Al_2O_3 ($\text{Cu/Al}_2\text{O}_3$) in place of the $\text{CuO-Al}_2\text{O}_3$ catalyst prepared by a co-precipitation method reported previously [20], in aqueous solvent with high acetic acid concentration on the benzene oxidation to phenol. The main aim of this study is to elucidate the influence of the Cu species, ascorbic acid, and the solvent on the activation of oxygen molecule in the oxygenation of benzene to phenol. The amount of the Cu species of a XRD peak observed at $2\theta = 23^\circ$ in the used $\text{Cu/Al}_2\text{O}_3$ catalyst had a correlation with the yield of phenol.

2. Experimental

2.1. Catalyst preparation

The Cu catalysts (Cu/oxide support) impregnated on Al_2O_3 (JRC- AlO_6), SiO_2 (JRC- SiO_8), TiO_2 (JRC- TiO_2), $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Nikki), MCM-41 (synthesized in this lab [23,24]), and HMCM-41 (synthesized in this lab [23,24]) were prepared by a conventional impregnation method using an aqueous solution of the prescribed concentration of $\text{Cu}(\text{CH}_3\text{COO})_2$. The resulting impregnated Cu catalysts

were dried at 393 K overnight and calcined at 773 K for 5 h in an air flow. The co-precipitated Cu catalyst ($\text{CuO-Al}_2\text{O}_3$) was prepared as follows: into an aqueous solution in which $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (Nacalai Tesque, guaranteed reagent, 0.57 g) and $\text{Al}(\text{NO}_3)_3$ (Nacalai Tesque, guaranteed reagent, 35.69 g) were homogeneously dissolved, 500 cm^3 of 1N aqueous Na_2CO_3 solution was added, and the mixture was stirred at 353 K for 3 h. The resulting precipitate was filtered-off under vacuum, washed with deionized water until the filtrate changed to pH 7, dried at 393 K overnight, and calcined at 623 K for 3 h in an air flow. The reduced $\text{CuO-Al}_2\text{O}_3$ catalyst was prepared by reducing at 553 K for 3 h under a H_2 flow. The amount of Cu on the $\text{CuO-Al}_2\text{O}_3$ catalyst was quantitatively measured by an atomic absorption spectrometer (Shimadzu Type AA-630-01) after homogeneously dissolving the catalyst by adding a few drop of hydrogen fluoride (Hashimoto Chemical, 47% content, guaranteed reagent). The (Zn-Cu)/ Al_2O_3 catalyst, the Cu and Zn of which were co-impregnated on an Al_2O_3 support was prepared using both $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{Zn}(\text{CH}_3\text{COO})_2$ (Nacalai Tesque, guaranteed reagent) followed by drying at 393 K overnight and calcining at 773 K for 5 h in flowing air. The reduced (Zn-Cu)/ Al_2O_3 catalyst was prepared by reducing at 553 K for 5 h in flowing H_2 . A Rb-added $\text{Cu/Al}_2\text{O}_3$ catalyst ($\text{Rb/Cu/Al}_2\text{O}_3$) was prepared by impregnating CH_3COORb (Nacalai Tesque, guaranteed reagent), drying at 393 K overnight, and calcining at 773 K for 5 h in flowing air.

2.2. Liquid-phase oxidation of benzene with the supported Cu catalysts

Benzene (Nacalai Tesque, guaranteed reagent) and acetic acid (Nacalai Tesque, guaranteed reagent) were used without further purification. Into a 50 cm^3 glass reactor, 2 cm^3 of benzene (22.5 mmol), 20 cm^3 of aqueous acetic acid (80 vol.%), 0.4 g catalyst, and the prescribed amount of a reductant were added. The reaction mixture was stirred magnetically at 303 K for 24 h under 0.1 MPa O_2 atmosphere. After adding 20 cm^3 of 2-propanol as an internal standard to the reaction solution, the reaction solution was separated from the solid catalyst by centrifugation. (2-Propanol was confirmed not to convert to acetone during the treatment.) The analyses of the oxidation product were performed at 453 K using a GLC (Shimadzu Type GC-8A) with a 3 m stainless column packed with Silicon OV-17 and a 1.5 m stainless column packed with 5% Thermon-3000 on SHIN-CARBON A. The quantitative analyses of the amount of the apparent Cu leaching were carried out by measuring the Cu amount dissolved in the filtrate using atomic absorption equipment (Shimadzu type AA-6200) after separating the solid catalyst from the reaction solution by centrifugation.

2.3. XRD measurement of supported Cu catalysts

The XRD patterns of both a fresh supported Cu catalyst and a used counterpart were measured at room temperature

using Rigaku Type Ultima⁺ XRD equipment with a Cu K α source. The used supported Cu catalyst separated through centrifugation was washed with acetone and either dried at around 383 K overnight or calcined at 773 K for 5 h in flowing air and subjected to XRD measurement.

2.4. Measurement of UV-Vis spectra

To investigate the generation of hydrogen peroxide, the UV-Vis absorption spectra of the aqueous solution including Cu(CH₃COO)₂ and ascorbic acid were measured at room temperature under air atmosphere using an electronic absorption spectrophotometer (Shimazu UV-240).

2.5. Liquid-phase adsorptions of benzene and phenol on Al₂O₃ support and the Cu/Al₂O₃ catalysts

A 1.0 g sample of the Al₂O₃ support or a Cu/Al₂O₃ catalyst was added to 20 cm³ of aqueous solution of 80 vol.% acetic acid including 2 cm³ of benzene or phenol. The whole system was stirred magnetically at 303 K for 24 h under N₂ atmosphere (0.1 MPa). After stirring, the benzene or phenol remaining in the solution was analyzed by GLC to quantitatively analyze the amount of benzene or phenol adsorbed on the Al₂O₃ support or the Cu/Al₂O₃ catalyst.

2.6. ESR spectra of the supported Cu catalysts

The ESR spectra of both the fresh and the used Cu/Al₂O₃ catalysts in a quartz cell were measured at room temperature using an ESR spectrometer (JES-TE-300). The fresh catalyst was degassed at 473 K for 2 h before ESR measurement. The used catalyst isolated centrifugally from the reaction solution was washed with acetone, dried at 373 K under N₂ flow, and degassed at 473 K for 2 h before the ESR measurement.

3. Results and discussion

3.1. Influences of both the supported Cu catalysts prepared under various conditions and the reaction conditions on the liquid-phase oxidation of benzene to phenol

The time dependence of both the yield of phenol and the percentage of Cu leaching was investigated using the co-precipitated Cu catalyst (CuO-Al₂O₃, Cu = 1.5 wt.%) in aqueous solvents with acetic acid concentrations of both 5.7 and 80 vol.% (Fig. 1(A)). The time dependence of the yield of phenol using the Cu catalyst impregnated on Al₂O₃ (Cu/Al₂O₃, Cu = 2 wt.%) in the aqueous solvent with 80 vol.% acetic acid is also illustrated in Fig. 1(B). No other products except phenol were detected under the reaction conditions studied in this report. The yields of phenol in both solvents increased with the reaction time up to around 2–3 h, but the extent of the increase in the phenol yield greatly declined beyond reaction times of around

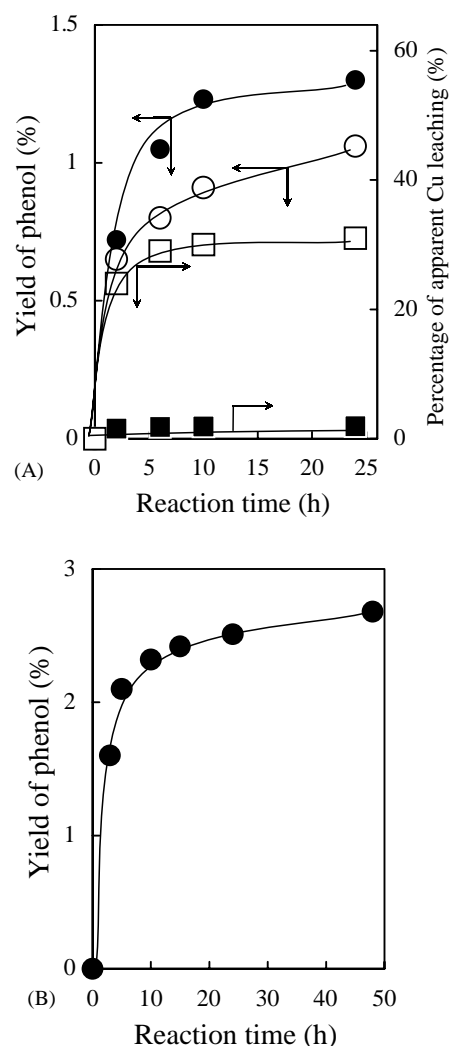


Fig. 1. Relationship of both yield of phenol and Cu leaching vs. reaction time. (A) Catalyst: 0.4 g of CuO-Al₂O₃ (Cu = 1.5 wt.%), (B) catalyst: 0.4 g of Cu/Al₂O₃ (Cu = 2 wt.%); ascorbic acid: 4 mmol; O₂: 0.1 MPa; reaction temperature: 303 K. (●), (■) 20 cm³ of aqueous solvent of 80 vol.% acetic acid; (○), (□) 20 cm³ of aqueous solvent of 5.7 vol.% acetic acid; (●), (○) yield of phenol; (■), (□) percentage of Cu leaching.

5 h, irrespective of the supported Cu catalysts. The yield of phenol over the CuO-Al₂O₃ catalyst using the aqueous solvent with the concentration of 80 vol.% acetic acid was higher than that using the counterpart with 5.7 vol.% acetic acid. The time dependence of both the percentages of the apparent Cu leaching showed behavior similar to those of both the yields of phenol. However, it must be noted that the apparent Cu leaching in the aqueous solvent with 80 vol.% acetic acid became remarkably lower than that in the aqueous solvent containing 5.7 vol.% acetic acid.

Fig. 2 illustrates the influence of the volumetric concentration of acetic acid in the aqueous acetic acid solvent on the yield of phenol at the reaction time of 24 h and the percentage of the apparent Cu leaching in the oxidation of benzene catalyzed by both the CuO-Al₂O₃ (Fig. 2(A)) and the Cu/Al₂O₃ (Fig. 2(B)). The yield of phenol increased with the

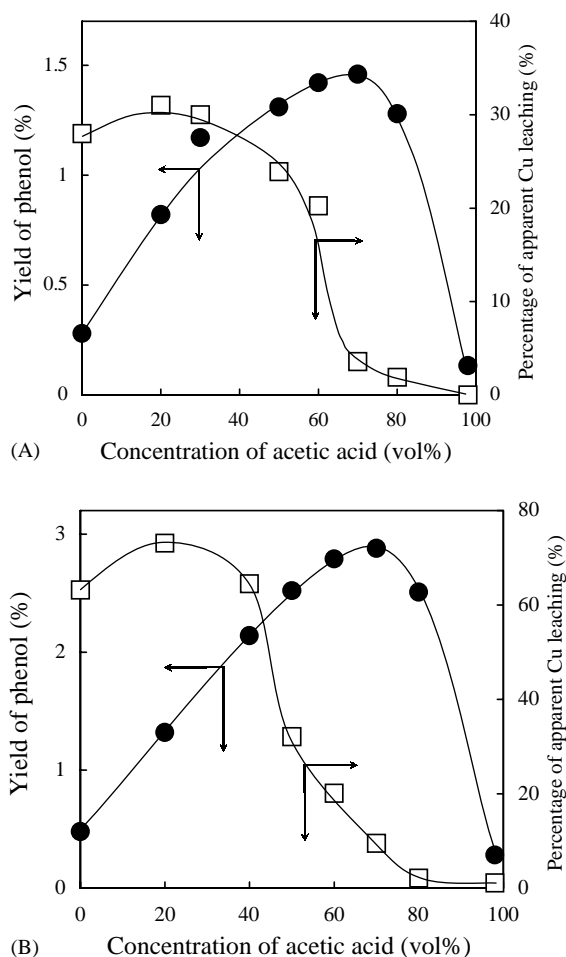


Fig. 2. Dependence of the concentration of acetic acid on both the yield of phenol and the Cu leaching. (A) Catalyst: 0.4 g of CuO-Al₂O₃ (Cu = 1.5 wt.%), (B) catalyst: 0.4 g of Cu/Al₂O₃ (Cu = 2 wt.%); benzene: 22.5 mmol; solvent: 20 cm³ of aqueous acetic acid; O₂: 0.1 MPa; ascorbic acid: 4 mmol; reaction temperature: 303 K; reaction time: 24 h. (●) Yield of phenol, (□) percentage of Cu leaching.

increase in the acetic acid concentration, but further increase in the acetic acid concentration inversely caused a decrease in the phenol yield and passed through a maximum value at a concentration of around 70 vol.%. The yield of phenol obtained in ca. 98 vol.% acetic acid solvent was somewhat lower than that in pure H₂O. The reason that the yield of phenol has an optimum value for the concentration of acetic acid will be interpreted by the following two factors. The reduction of Cu²⁺ to Cu⁺, of which the reduced Cu species are indispensable for phenol formation [17–20], by ascorbic acid will be inhibited in the strong acid medium [25]. On the other hand, the production of H₂O₂ by the reduction of O₂ with the Cu⁺ will be promoted in acid medium, and the produced H₂O₂ can be stably present in the acid medium [26]. Thus, the trade-off between the ease of the reduction of Cu²⁺ to Cu⁺, and the effective production and the stability of the produced H₂O₂ might result in an optimum aqueous solvent with an acetic acid concentration of around 70 vol.%. The percentage of the apparent Cu leaching remained almost constant (around 30% for CuO-Al₂O₃ and 40 vol.% for Cu/Al₂O₃) up to acetic acid concentrations of ca. 30–40 vol.%. Further increase in the acetic acid concentration caused a gradual decrease in the percentage of apparent Cu leaching. Surprisingly, acetic acid concentrations of more than around 40–60 vol.% caused a sharp decrease in the percentage of apparent Cu leaching. On the other hand, the yield of phenol hardly decreased up to acetic acid concentrations of around 80 vol.% as illustrated in Fig. 2(A) and (B). The aqueous solvent containing high acetic acid was thus confirmed to inhibit the apparent Cu leaching from the Cu catalyst (Cu/Al₂O₃) impregnated on Al₂O₃, as well as the CuO-Al₂O₃ catalyst reported previously [20], keeping the phenol yield comparatively high.

Table 1 indicates the yield of phenol and the percentage of apparent Cu leaching for the Cu catalysts impregnated on various oxide supports using aqueous solvents of both 20 and 80 vol.% acetic acid. Only phenol was detected as the

Table 1

Influence of oxide supports on the yield of phenol and the percentage of apparent Cu leaching using the aqueous solvent of both 20 and 80 vol.% acetic acids^a

Catalyst	Acetic acid (20 vol.%)		Acetic acid (80 vol.%)	
	Yield of phenol (%)	Apparent Cu leaching (%)	Yield of phenol (%)	Apparent Cu leaching (%)
Cu/SiO ₂	0.9	57.1	1.4	1.8
Cu/TiO ₂	0.4	42.3	0.6	1.0
Cu/Al ₂ O ₃	1.4	73.8	2.5	1.7
Cu/SiO ₂ -Al ₂ O ₃	1.0	68.5	2.1	2.3
Cu/MCM-41 (Si/Al = ∞)	1.1	64.5	1.6	2.1
Cu/MCM-41 (Si/Al = 108)	1.3	69.2	1.7	2.1
Cu/MCM-41 (Si/Al = 69)	1.6	58.3	2.1	3.2
Cu/MCM-41 (Si/Al = 26)	1.5	62.2	2.5	3.1

^a Reaction conditions: Cu content, 2 wt.%; benzene, 22.5 mmol; solvent, aqueous acetic acid, 20 cm³; O₂, 0.1 MPa; ascorbic acid, 4 mmol; reaction temperature, 303 K; reaction time, 24 h.

oxidation product for all the supported Cu catalytic systems studied here. The yield of phenol using the aqueous solvent of 80 vol.% acetic acid was higher than that using 20 vol.% acetic acid regardless of the oxide supports. Once again, the percentages of apparent Cu leaching in the aqueous solvent of 80 vol.% acetic acid considerably declined in comparison with those in 20 vol.% acetic acid. Thus, the aqueous solvent with a high acetic acid concentration of around 80 vol.% was confirmed to be eligible to both phenol production and the inhibition of apparent Cu leaching. The aqueous acetic acid solvent with the acetic acid concentration of around 80 vol.% was thus found to be an optimum solvent maintaining both a comparatively high yield of phenol and a low level of apparent Cu leaching.

The dependence of the amount of the supported Cu on the yield of phenol was investigated using the Cu/Al₂O₃ catalyst in aqueous solvent of an acetic acid concentration of 80 vol.% (Fig. 3). The yield of phenol sharply increased with the increase in the amount of the supported Cu up to around 3 wt.%, but further increase in the Cu amount inversely caused a decline in the yield of phenol. Too high an amount of the supported Cu may not function effectively for phenol formation because of the aggregation of Cu species on the Al₂O₃ support. In fact, the ESR spectrum of the used Cu/Al₂O₃ (Cu = 20 wt.%) catalyst was characteristic of aggregated Cu species [27] (not depicted). The percentage of apparent Cu leaching remained at low values regardless of the amount of the supported Cu.

The influence of the calcination temperature of the Cu/Al₂O₃ catalyst on the constant amount of the supported Cu of 2 wt.% is illustrated in Fig. 4. The calcination temperatures in the range of 573–973 K caused little change in the yield of phenol. However, the apparent Cu leaching

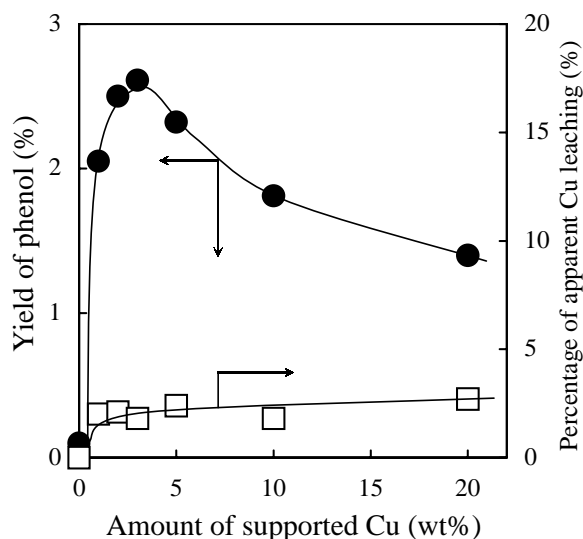


Fig. 3. Dependence of the amount of supported Cu on the yield of phenol and the percentage of Cu leaching. Catalyst: 0.5 g of Cu/Al₂O₃; benzene: 22.5 mmol; solvent: 20 cm³ of aqueous 80 vol.% acetic acid; O₂: 0.1 MPa; ascorbic acid: 4 mmol; reaction temperature: 303 K; reaction time: 24 h.

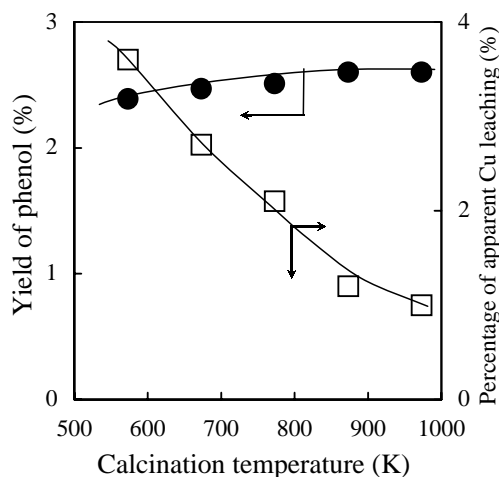


Fig. 4. Influence of calcination temperature on both the yield of phenol and percentage of Cu leaching. Catalyst: 0.4 g of Cu/Al₂O₃ (Cu = 2 wt.%); benzene: 22.5 mmol; solvent: 20 cm³ of aqueous 80 vol.% acetic acid; ascorbic acid: 4 mmol; reaction temperature: 303 K; reaction time: 24 h. (●) Yield of phenol, (□) percentage of Cu leaching.

was moderately inhibited by calcining the catalyst at higher temperatures. The yield of phenol and the percentage of apparent Cu leaching for the Cu/Al₂O₃ catalyst only dried at 393 K overnight were 2.3 and 6.8%, respectively.

The influence of the amount of ascorbic acid as a reducing reagent on the yield of phenol was investigated using both the Cu/Al₂O₃ (Cu = 1.5 wt.%) and the CuO-Al₂O₃ (Cu = 1.5 wt.%) catalysts (Fig. 5) in the aqueous solvent with 80 vol.% acetic acid. The result [20] of the CuO-Al₂O₃ (Cu = 3.0 wt.%) catalyst in the aqueous solvent with 5.7 vol.%

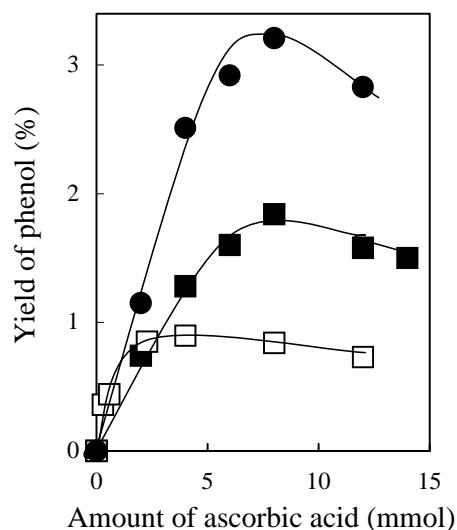


Fig. 5. Influence of amount of ascorbic acid on the yield of phenol. (●) Cu/Al₂O₃ catalyst (Cu = 2 wt.%) in 20 cm³ of aqueous 80 vol.% acetic acid, (■) CuO-Al₂O₃ (Cu = 1.5 wt.%) in 20 cm³ of aqueous 80 vol.% acetic acid, (□) CuO-Al₂O₃ (Cu = 3 wt.%) in 20 cm³ of aqueous 5.7 vol.% acetic acid ([16]). Catalyst: 0.4 g of Cu/Al₂O₃; benzene: 22.5 mmol; reaction temperature: 303 K; reaction time: 24 h for (●) and (■), 5 h for (□).

acetic acid is also plotted as a reference. The CuO-Al₂O₃ catalyst in the aqueous solvent with 80 vol.% acetic acid had higher catalytic activity than that in the solvent with 5.7 vol.% acetic acid, in spite of the fact that the Cu content of the latter catalyst was twice that of the former. The yield of phenol increased with the increase in the amount of ascorbic acid, but too large an amount of ascorbic acid tended to inversely decrease the yield of phenol on both catalysts. The excess amount of ascorbic acid is suggested to decompose H₂O₂ produced during the benzene oxidation, rather than being effectively available for phenol formation. To ascertain the behavior of ascorbic acid toward H₂O₂, the variation in the electronic absorption spectra of aqueous H₂O₂ (8.8×10^{-3} mol/l) solution by adding an aqueous solution of ascorbic acid (8.0×10^{-4} mol/l) was observed. The peak at around 200 nm based on H₂O₂, together with the peak intensity of the ascorbic acid at 260 nm, was confirmed to decrease with time. The stability of H₂O₂, formed during the oxidation of benzene catalyzed by the supported Cu catalysts in an acid medium may be the reason why the maximum value of the phenol yield shifted to a higher amount of ascorbic acid in the aqueous solvent with 80 vol.% acetic acid concentration than that with 5.7 vol.% acetic acid.

The influence of rubidium (as an oxide) added to the Cu/Al₂O₃ (Cu = 2 wt.%) catalyst on the benzene oxidation to phenol was investigated using the Rb/Cu/Al₂O₃ catalysts with the added Rb/Cu atomic ratios of 1, 5, and 10. The Rb/Cu/Al₂O₃ catalyst with the added Rb/Cu ratio of 1 slightly promoted the phenol formation (the phenol yields of the Cu/Al₂O₃ and the Rb/Cu/Al₂O₃ catalysts were 2.5 and 2.75%, respectively) but the catalysts with the ratios of 5 and 10 inversely inhibited the phenol formation (both the phenol yields were 2.3%). The zinc co-impregnated Cu/Al₂O₃ catalyst [(Zn-Cu)/Al₂O₃] was attempted as a catalyst for the liquid-phase benzene oxidation to investigate if the added zinc metal functions as a reducing reagent, but the impregnated Zn had no effect as a reducing reagent for the phenol formation.

3.2. Apparent Cu leaching from the supported Cu catalyst in the aqueous solvents with concentrations of both high and low acetic acid

Whenever a supported metal catalyst is utilized in a liquid-phase reaction, a concomitant concern is the leaching of the supported metal ion into the reaction solution during the catalytic reaction. The use of an aqueous solvent with acetic acid of high concentrations was found to considerably inhibit the apparent leaching of Cu (Fig. 2). The Cu species leached into the reaction solution from the catalyst will be reduced to Cu⁺ ions during the benzene oxidation in the presence of ascorbic acid [17–20], the reduced Cu⁺ species of which will hardly be soluble in the aqueous reaction solution. Because the reduced Cu⁺ species are insoluble in the reaction solution and precipitate during the benzene oxidation, the sharp decline in the percentage of

Table 2

Percentage of apparent Cu leaching from the CuO-Al₂O₃ catalyst in various solutions^a

Concentration of acetic acid in solvent (vol.%)	Only solvent (%)	Solution		
		Benzene (%)	Ascorbic acid (%)	Benzene + ascorbic acid (%)
5.7	65.3	60.2	33.0	31.0
80	6.3	4.4	1.9	1.9

^a Reaction conditions: catalyst, CuO-Al₂O₃ (Cu = 1.5 wt.%), 0.4 g; solvent, 20 cm³ of aqueous acetic acid; benzene, 22.5 mmol (2 cm³); ascorbic acid, 4 mmol; temperature, 303 K; treating time, 24 h; O₂, 0.1 MPa.

the Cu leaching at acetic acid concentrations of more than around 40–60 vol.% observed in Fig. 2 may be only an apparent value, because the percentages of the Cu leaching were obtained by measuring the homogeneous Cu species soluble in the reaction solution. The influence of ascorbic acid and/or benzene present in the aqueous acetic acid solution on the apparent Cu leaching of the CuO-Al₂O₃ catalyst was investigated using aqueous solutions with acetic acid concentrations of both 5.7 and 8 vol.% (Table 2), where the percentage of the apparent Cu leaching was measured after stirring for 24 h at 303 K under each condition described in Table 1. The percentage of apparent Cu leaching in aqueous acetic acid solvent containing no ascorbic acid was considerably different for the concentrations of acetic acid of 5.7 and 80 vol.%. Thus, the aqueous solvent with acetic acid of a high concentration (80 vol.%) caused a much lower Cu leaching than that with acetic acid of a low concentration (5.7 vol.%). The percentages of the apparent Cu leaching in the presence of only ascorbic acid using both the 5.7 and 80 vol.% acetic acid concentrations were very similar to those obtained in the solution including both benzene and ascorbic acid (in which solution the benzene oxidation proceeds). The apparent Cu leaching in the latter two systems containing ascorbic acid were lower than those in the former two systems not containing ascorbic acid, irrespective of the acetic acid concentration of 5.7 and 80 vol.%. The difference in the Cu leaching between both the systems containing and not containing ascorbic acid will be due to the contribution of the Cu⁺ species reduced by ascorbic acid to the apparent decline of the percentage of the Cu leaching. The result that the apparent Cu leaching in the aqueous solution with acetic acid of high concentrations was thus considerably lower than that in acetic acid of low concentrations, irrespective of the presence of ascorbic acid, indicates that the aqueous solvent with high acetic acid concentration can intrinsically inhibit the Cu leaching, though the contribution of the insoluble Cu⁺ reduced by ascorbic acid cannot be ignored as described previously.

3.3. Deactivation of the Cu/Al₂O₃ catalyst and its regeneration

The reuse of the Cu/Al₂O₃ catalyst was attempted after the used catalyst washed with acetone was either only dried

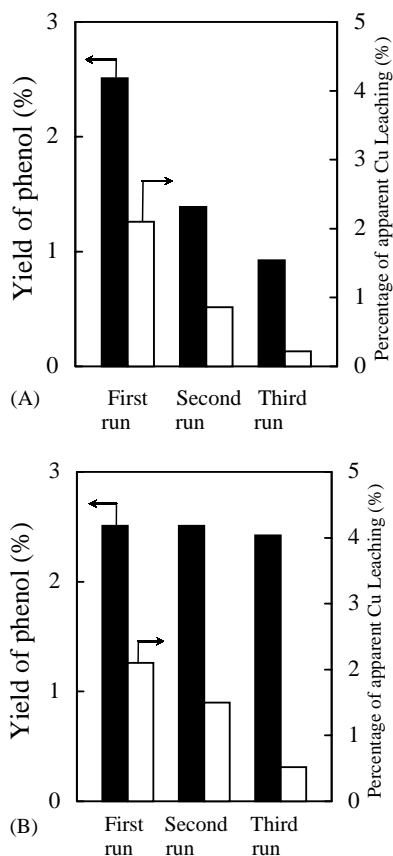


Fig. 6. Reuse of the Cu/Al₂O₃ catalyst in the oxidation of benzene. Catalyst: 0.4 g of Cu/Al₂O₃ (Cu = 2 wt.%); benzene: 22.5 mmol; solvent: 20 cm³ of aqueous 80 vol.% acetic acid; ascorbic acid: 4 mmol; reaction temperature: 303 K; reaction time: 24 h. (A) Reuse of the catalyst after drying at 393 K overnight, (B) reuse of the catalyst after calcining at 773 K for 5 h in flowing air.

at 393 K overnight or calcined at 773 K for 5 h (Fig. 6). The catalytic activity of the reused catalyst treated only by drying largely decreased with repeated use (Fig. 6(A)). On the other hand, the yield of phenol obtained by the third reaction was almost similar to that of the first one when the used catalyst was dried at 393 K followed by calcination at 773 K (Fig. 6(B)). The apparent Cu leaching was inhibited with repeated usage of the catalyst, regardless of the treatment method for the used catalyst.

As described previously, the yield of phenol leveled-off at a reaction time of around 5–10 h and hardly increased with a further increase in the reaction time, irrespective of the supported Cu catalysts (Fig. 1). Based on these results, the adsorption of the produced phenol on the catalyst surface will be considered one of the causes of deactivation. However, the liquid-phase adsorption experiment of phenol confirmed that the phenol hardly adsorbed on either the Cu/Al₂O₃ catalyst or Al₂O₃ support under conditions similar to the benzene oxidation.

To investigate another cause of the deactivation, XRD measurements of both the fresh and the used Cu/Al₂O₃ (Cu

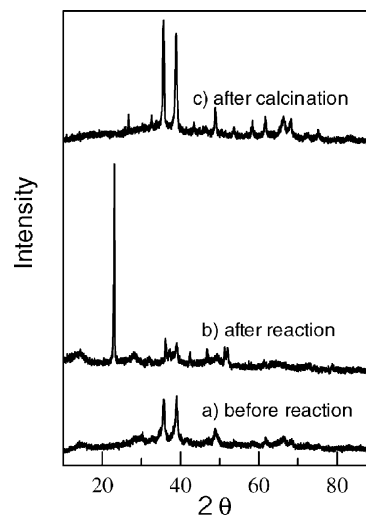


Fig. 7. XRD patterns of Cu/Al₂O₃ catalysts. (a) Fresh Cu/Al₂O₃ catalyst, (b) used Cu/Al₂O₃ catalyst, (c) used Cu/Al₂O₃ (b) calcined at 773 K for 5 h in flowing air.

= 20 wt.%) catalysts were carried out (Fig. 7). The intensity of the XRD pattern based on CuO of the used catalyst became lower than that of the fresh one. The ESR spectra (not illustrated) of both the fresh and the used catalysts showed that the ESR peaks based on Cu²⁺ of the latter catalyst became lower than that of the former, in accordance with the XRD data. However, a marked difference in both the XRD patterns is the appearance of a sharp peak at $2\theta = 23^\circ$ in the used catalyst (Fig. 7(b)). The new XRD peak was not identical with those of Cu powder, Cu₂O, CuO, copper(II) acetate, copper(II) hydroxide, and copper(II) carbonate. The Cu precipitate produced from a mixture of copper(II) acetate and ascorbic acid in aqueous acetic acid of 80 vol.% showed an XRD peak at $2\theta = 23^\circ$ (Fig. 8(a)) that was exactly the same as that which appeared in the used Cu/Al₂O₃ catalyst (Fig. 8(b)). Thus, the Cu species based on the XRD peak

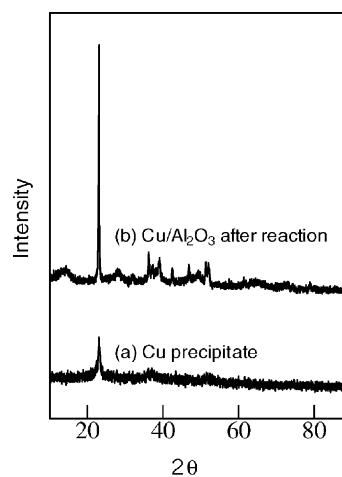


Fig. 8. XRD patterns of the precipitate and the Cu/Al₂O₃ catalyst. (a) Cu precipitate formed from the mixture of copper acetate and ascorbic acid in acetic acid, (b) used Cu/Al₂O₃ (same as in Fig. 7(b)).

at $2\theta = 23^\circ$ will be due to the reduced Cu species. We are now exploring the identification of the Cu species based on the XRD peak at $2\theta = 23^\circ$ and will report the results in the near future, though we have no knowledge yet of a definite formula for the Cu precipitate. The calcination of the used Cu/Al₂O₃ catalyst at 773 K for 5 h in flowing air resulted in both the disappearance and an increase in the intensity of the XRD peaks based on CuO (Fig. 7(c)). From these XRD data, the active Cu species is thought to irreversibly convert to inactive Cu species during the benzene oxidation, and the deactivated Cu species will be reactivated through the calcination treatment, as shown in Fig. 6.

To confirm that the precursors of the Cu species based on the XRD peak at $2\theta = 23^\circ$ are related to the active species for phenol formation, the XRD measurement of the used Cu/Al₂O₃ catalysts prepared in aqueous solution with various acetic acid concentrations was attempted. The height of the XRD peak at $2\theta = 23^\circ$, together with the yield of phenol, was plotted against the volumetric concentration of acetic acid (Fig. 9). A correlation between the yield of phenol and the intensity of the XRD peak at $2\theta = 23^\circ$ was observed against the volumetric concentration of acetic acid. Thus, the deactivated Cu species based on the XRD peak at $2\theta = 23^\circ$ will be formed via the active Cu species for phenol formation, although the composition and the structure of the deactivated Cu species are yet unknown at the present stage.

3.4. Hydrogen peroxide formation from an aqueous solution of Cu²⁺ and ascorbic acid in air and the activity for phenol formation

Hydrogen peroxide accumulated during the liquid-phase oxidation of benzene by Cu supported MCM-41 (Cu/MCM-41) catalyst using ascorbic acid as a reducing reagent was

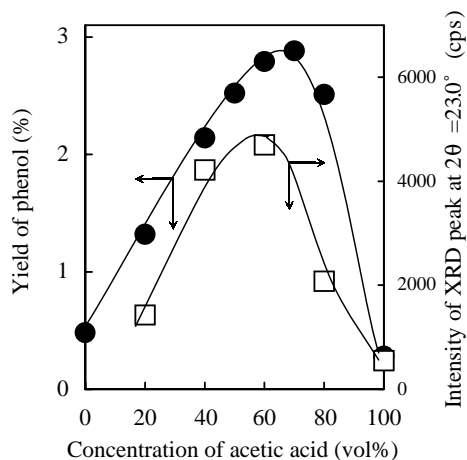


Fig. 9. Dependence of concentration of acetic acid on both the yield of phenol and intensity of the XRD peak at $2\theta = 23^\circ$. Catalyst: 0.4 g of Cu/Al₂O₃ (Cu = 2 wt.%); benzene: 22.5 mmol; solvent: 20 cm³ of aqueous acetic acid; O₂: 0.1 MPa; ascorbic acid: 4 mmol; reaction temperature: 303 K; reaction time: 24 h. (●) Yield of phenol, (□) intensity of XRD peak at $2\theta = 23^\circ$.

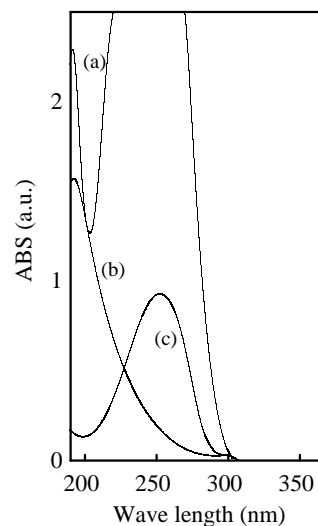


Fig. 10. Electronic absorption spectra of H₂O₂ generated from aqueous solution containing both Cu²⁺ and ascorbic acid. (a) Aqueous solution containing both Cu acetate (2.2×10^{-5} mol/l) and ascorbic acid (8.0×10^{-4} mol/l), (b) aqueous solution of H₂O₂ (8.8×10^{-4} mol/l), (c) aqueous solution of ascorbic acid (8.0×10^{-4} mol/l).

quantitatively analyzed by conventional iodometry [18]. To directly observe whether H₂O₂ is formed in the presence of oxygen (air), ascorbic acid, and the Cu/Al₂O₃ catalyst, the UV-Vis spectrum of the aqueous solution including Cu(II) acetate and ascorbic acid was measured, in addition to those of aqueous solutions of only ascorbic acid and H₂O₂ (Fig. 10). Copper(II) acetate was utilized, in place of the Cu/Al₂O₃ catalyst, because the Cu²⁺ species leached from the Cu/Al₂O₃ catalyst, together with the Cu species supported on the catalyst, are considered to play a role in H₂O₂ formation. An absorption peak was detected at around 200 nm (Fig. 10(a)), the peak of which is identical of that of authentic aqueous H₂O₂ (Fig. 10(b)), when the aqueous solutions of the Cu²⁺ and ascorbic acid were mixed in air. Benzene oxidation was attempted under a variety of conditions with and without H₂O₂ to investigate the role of the reducing reagent (ascorbic acid) and the oxidant for phenol formation (Table 3). In the absence of H₂O₂, the presence

Table 3
Influence of oxidant and reducing reagent on the phenol formation^a

Run	H ₂ O ₂ (mmol)	Ascorbic acid (mmol)	Atmosphere	Yield of phenol (%)
1	0	0	N ₂	0
2	0	0	O ₂	0
3	0	4	O ₂	2.5
4	0	4	N ₂	0
5	9.6	4	O ₂	1.2
6	9.6	0	N ₂	0
7	9.6	0	O ₂	0.2

^a Reaction conditions: catalyst, Cu/Al₂O₃ (Cu = 2 wt.%), 0.4 g; benzene, 22.5 mmol; solvent, 20 ml of aqueous acetic acid (80 vol.%); reaction pressure, 0.1 MPa; reaction temperature, 303 K; reaction time, 24 h.

of Cu species, ascorbic acid and O₂, followed by the formation of H₂O₂ as described previously (Fig. 10), are essential to phenol formation (Run 3). Contrary to our expectation, no phenol was detected in the presence of H₂O₂ and in the absence of both ascorbic acid and O₂ under the present reaction condition (Run 6). Only small amount of phenol was produced in the presence of both H₂O₂ and O₂ and in the absence of ascorbic acid (Run 7). From the results of Table 3, the O₂ and ascorbic acid may be necessary for the generation of hydroxyl radical from hydrogen peroxide, though we do not have the mechanism of the formation of hydroxyl radical.

4. Conclusions

An aqueous solvent with high acetic acid concentration was confirmed to be an effective medium for the benzene oxidation catalyzed by a supported Cu catalyst. The benefits of both a comparatively high yield of phenol and a low apparent Cu leaching was simultaneously obtained using a Cu catalyst impregnated on Al₂O₃ (Cu/Al₂O₃), as well as a CuO-Al₂O₃ catalyst prepared by a co-precipitation method reported previously [20], in the aqueous solvent with high acetic acid concentrations (around 70–80 vol.%). The apparent Cu leaching from the Cu/Al₂O₃ catalyst during the benzene oxidation dramatically decreased using the aqueous solvent with acetic acid concentrations of more than around 70 vol.%. However, too high a concentration of acetic acid (more than 80 vol.%) caused a sharp decrease in the yield of phenol. The yield of phenol had a maximum value at an amount of the supported Cu of ca. 2 wt.%, and a further increase in the amount of the supported Cu caused a decrease in the yield of phenol. The aggregated Cu species on the Cu/Al₂O₃ catalyst observed from the ESR spectra was suggested to inhibit the formation of phenol. The phenol yield increased with an increase in the amount of ascorbic acid and passed through a maximum value using both the Cu/Al₂O₃ and CuO-Al₂O₃ catalysts in the aqueous solvent with 80 vol.% acetic acid. The formation of hydrogen peroxide was observed in the electronic absorption spectra of the aqueous solution in the presence of Cu²⁺ ion, ascorbic acid, and O₂. The used Cu/Al₂O₃ catalyst had a new XRD peak at $2\theta = 23^\circ$. Both the peak intensity at $2\theta = 23^\circ$ and the yield of phenol had a similar dependence on the volumetric concentration of acetic acid in the aqueous solvent. The deactivated Cu species based on the XRD peak at $2\theta = 23^\circ$ will be thus formed via the active Cu species for phenol formation. The calcinations of the used Cu/Al₂O₃ catalyst caused the disappearance of the XRD peak at $2\theta = 23^\circ$ and the recovery of the catalytic activity for the phenol formation.

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