

Liquid-phase oxidation of benzene to phenol by vanadium catalysts in aqueous solvent with high acetic acid concentration

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Abstract

The synthesis of phenol through the direct oxygenation of benzene was attempted using supported vanadium catalysts in aqueous acetic acid solvent. Gaseous oxygen and ascorbic acid were used as an oxidant and a reducing reagent, respectively. The yield of phenol increased with the increase in the concentration of acetic acid in the aqueous solvent, and had a maximum value at the acetic acid concentration of around 80 vol.%. The influences of the partial pressure of O₂ and the amount of ascorbic acid on the yield of phenol were investigated using V/Al₂O₃ catalyst in the aqueous solvent containing 80 vol.% acetic acid. The oxidation of benzene catalyzed by V/Al₂O₃ using hydrogen peroxide as an oxidant instead of gaseous oxygen indicated that the yield of phenol increased with the increase in the concentration of acetic acid in the aqueous solvent. The supported vanadium catalyst with added zinc had a catalytic activity for phenol formation, though the yield was low, even in the absence of ascorbic acid. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

More than 90% of the industrial production of phenol is done using the cumene process, which consists of three steps and produces acetone as a byproduct. One of the advantages of this process is that each selectivity of the three steps is more than 90%. The concomitant dependence of the byproduct, acetone, on the chemical market will become a drawback in this process.

The liquid-phase direct hydroxylation of benzene has been reported by Dixon and Norman [1] using ferrous sulfate–H₂O₂ system (Fenton reagent). Recently, direct oxidation of benzene using oxygen species

obtained by activating molecular oxygen by reducing reagent has been attempted by various catalytic systems. The oxidation of benzene to phenol has been reported [2] using EuCl₃ or VO(acac)₂ catalyst and Zn as a reducing reagent in an aqueous acetic acid solvent. Hetero polyacid, which was partly exchanged, has been attempted [3,4] as a catalyst for the direct oxidation of benzene to phenol using H₂O₂ oxidant.

We have attempted the liquid-phase oxidation of benzene to phenol catalyzed by Cu-supported zeolites [5,6] and Cu-supported MCM-41 catalysts [7] using both gaseous oxygen as an oxidant and ascorbic acid as a reducing reagent. Vanadium catalyst supported on SiO₂ has also been utilized [8] for liquid-phase oxidation of benzene to phenol using both gaseous O₂ and ascorbic acid.

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In extending the study on the supported vanadium catalyst for liquid-phase benzene oxidation, the catalytic activity for phenol formation of the supported vanadium catalyst was found to be considerably promoted using the catalyst in an aqueous solvent containing high acetic acid. This paper reports the catalytic behavior of the supported vanadium catalyst (mainly vanadium catalyst supported on Al_2O_3) for the liquid-phase oxidation of benzene under the various reaction conditions. The effectiveness of the aqueous solvent with high concentration of acetic acid will be interpreted as the effective utilization of hydrogen peroxide, which was suggested to be an important intermediate for phenol formation, in the higher concentration of acetic acid.

2. Experimental

2.1. Catalyst preparation

SiO_2 (JRC-SiO8), TiO_2 (JRC-TiO2), and Al_2O_3 (JRC-ALO4) were obtained from Japan Catalysis Society. NaY (Toso) was commercially available. MCM-41 was synthesized according to the literature [7]. A supported vanadium catalyst was usually prepared by the impregnation method using a prescribed concentration of bis(acetylacetonato)oxovanadium ($\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$) (Nacalai Tesque, guaranteed reagent) ethanolic solution. After the evaporation of the solvent, the supported vanadium was dried at 393 K overnight and calcined at 623 K for 3 h in flowing air. V and Zn co-impregnated Al_2O_3 catalyst ((V–Zn)/ Al_2O_3) was prepared using Al_2O_3 as a support and the ethanolic solution containing both 2 wt.% $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ and a prescribed amount of $\text{Zn}(\text{CH}_3\text{COO})_2$ (Zn/V atomic ratio = 0.2–20). A small amount of oxalic acid was added in advance because of the poor solubility of zinc acetate. The obtained (V–Zn)/ Al_2O_3 was dried at 393 K overnight and calcined at 623 K for 3 h in flowing air. The reduced (V–Zn)/ Al_2O_3 was prepared by reducing the (V–Zn)/ Al_2O_3 at 773 K for 3 h in H_2 flow.

2.2. Liquid-phase oxidation of benzene

The liquid-phase oxidation of benzene was carried out using a stainless steel reactor (Taiatsu glass, i.d.:

1.7 cm; height: 11.2 cm) with a magnetic stirrer. The standard reaction condition is as follows: 5 cm^3 of aqueous solvent containing a prescribed amount of acetic acid, 5.6 mmol (0.5 cm^3) of benzene, 1 mmol of ascorbic acid, 0.4 MPa of oxygen, reaction temperature of 303 K, and reaction time of 24 h. The benzene oxidation using H_2O_2 as an oxidant, in place of gaseous O_2 , was performed in a similar manner, except for N_2 atmosphere (0.4 MPa). The reaction mixture, in which 5 cm^3 of propanol-2 was added as an internal standard, was centrifugally separated from the solid catalyst. The obtained reaction solution was transferred to GLC analysis. The detail in the analytical method was described elsewhere [8]. The benzene oxidation using unsupported vanadium catalysts ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, VCl_3 , $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$, NH_4VO_3 , V_2O_5) was also conducted under the same reaction conditions as the oxidation using the V/ Al_2O_3 catalyst. The amount of V leached in the reaction solution was analyzed using an atomic absorption spectrometer (Shimadzu Type AA-630-01).

2.3. Quantitative analysis of hydrogen peroxide

The H_2O_2 that accumulated or remained during the reaction was quantitatively analyzed by idometry [9]. The solid catalyst was centrifuged from the reaction solution before transforming to the idometry. A small amount of sodium bicarbonate was added to the solution during the titration to prevent the autooxidation of I^- ions in the acidic titration solution.

2.4. Electronic absorption spectra of the reaction solution

Electronic absorption spectra was measured using an electronic absorption spectrophotometer (Shimadzu Model UV-240) at room temperature.

3. Results and discussion

3.1. Benzene oxidation to phenol by supported and unsupported V catalysts in aqueous solvent with high acetic acid concentration

Supported Cu catalysts in aqueous solvent with high acetic acid concentration (around 70–80 vol.%)

have been found [10] to give both higher phenol yield and lower leaching of Cu for the liquid-phase oxidation of benzene using gaseous oxygen and ascorbic acid as an oxidant and a reducing reagent, respectively. The catalytic activities for benzene oxidation of the V catalysts supported on some oxides have been already reported [8] using aqueous solvent with acetic acid of comparatively low volumetric concentration (5.7 vol.% (1 M acetic acid concentration)). The variation in the pH of the reaction solution has also been reported [11] to bring the change in the product distribution of Fenton-type reaction.

The influence of volumetric concentration of acetic acid in the aqueous solvent on both the yield of phenol and the leaching of V was investigated using both V/SiO₂ and V/Al₂O₃ catalysts (Figs. 1A and B). Phenol was also formed, although the yield was not high using the catalysts in water solvent without acetic acid. The increase in acetic acid using both the V/SiO₂ and V/Al₂O₃ catalysts caused a considerable increase in the yield of phenol until the volumetric concentration of acetic acid of around 80%, but further increase in acetic acid rapidly reduced the yield of phenol. The percentage of the V leaching did not vary so largely with the variation of the volumetric concentration of acetic acid in both V/SiO₂ and V/Al₂O₃ catalysts. The yield of phenol obtained in this study will be basically evaluated as a sum of the yields produced from the heterogeneous and the soluble catalytic parts because the contribution of the leaching V species cannot be ignored.

To investigate the contribution of leached vanadium species to the phenol formation, benzene oxidation using some unsupported vanadium species in place of the V/Al₂O₃ catalyst, was attempted. The activities for phenol formation of both supported (V/Al₂O₃) and unsupported vanadium catalysts were almost similar under the same reaction conditions (V amounts in V/Al₂O₃ and unsupported catalyst was 3.9 and 4 mmol, respectively, solvent: 5 cm³ of aqueous solvent containing 80 vol.% acetic acid; ascorbic acid: 1 mmol; benzene: 5.6 mmol; O₂ pressure: 0.4 MPa; reaction temperature, 303 K; reaction time, 24 h): phenol yields by supported V/Al₂O₃ catalyst, 8.2%; phenol yields by unsupported VOSO₄·5H₂O, VCl₃, VO(C₅H₇O₂)₂, NH₄VO₃, and V₂O₅ catalysts were 5.1, 8.2, 8.2, 9.8, and 7.6%, respectively. The yields of phenol catalyzed by both the unsupported NH₄VO₃

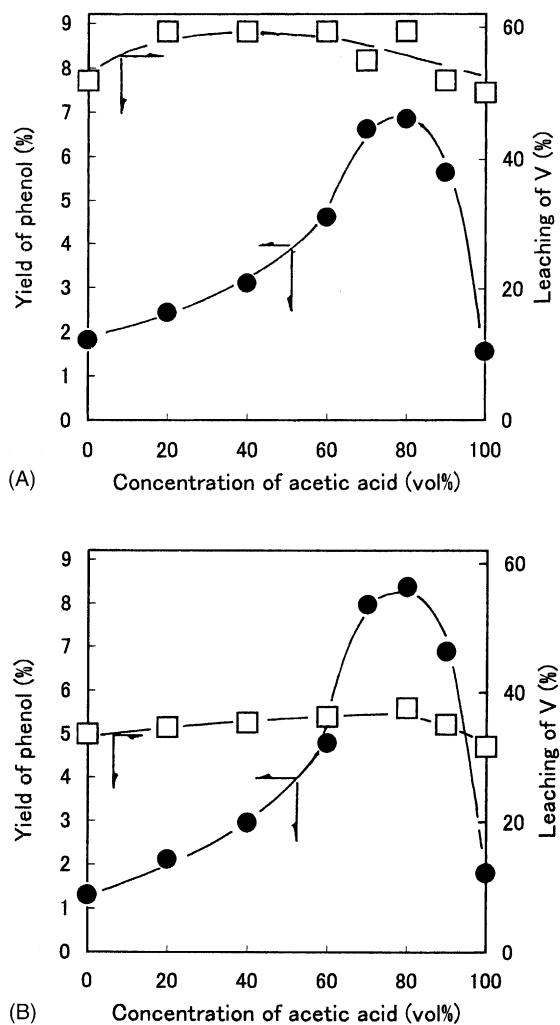


Fig. 1. Influence of volumetric concentration of acetic acid on both yield of phenol and leaching of V. Benzene, 5.6 mmol; O₂, 0.4 MPa; ascorbic acid, 1 mmol; solvent, 5 cm³ of aqueous acetic acid; reaction temperature, 303 K; reaction time, 24 h; ●, yield of phenol; □, leaching of V; (A) V/SiO₂ (V: 2 wt.%) catalyst, 0.1 g; (B) V/Al₂O₃ (V: 2 wt.%), 0.1 g.

and VO(C₅H₇O₂)₂ catalysts were also confirmed to have a maximum value in aqueous solvent containing ca. 70–80 vol.% of acetic acid. It is inferred from these results of both the supported and the unsupported vanadium catalysts that the catalytic function of the vanadium species of both the unsupported catalyst and on the supported one is substantially similar for phenol formation.

Table 1

Benzene oxidation with supported V catalysts in aqueous 80 vol.% acetic acid solvent^a

Catalyst	Yield of phenol (%)	Leaching of V (%)
V/SiO ₂ ^b	2.5	80.0
V/SiO ₂	6.6	59.3
V/MCM-41	8.6	61.0
V/Al ₂ O ₃	8.2	37.6

^a Catalyst: 0.1 g (V=2 wt.% (0.39 mmol V/g_{cat.})), benzene: 5.6 mmol, solvent: 5 cm³ of aqueous solution containing 80 vol.% of acetic acid, reducing reagent: 1 mmol of ascorbic acid, O₂ pressure: 0.4 MPa, reaction temperature: 303 K.

^b Ref. [8], solvent: 5 cm³ of aqueous 5.7 vol.% acetic acid.

The results obtained using three supported V catalysts in aqueous 80 vol.% acetic acid solvent as catalysts for benzene oxidation are summarized in Table 1. The catalytic activity of the supported V catalysts for phenol formation was promoted by ca. 2.5–3.5 times using the aqueous solvent containing 80 vol.% acetic acid, instead of 5.7 vol.% (1 M) acetic acid [8]. It is noteworthy that the degree of V leaching from the supported V catalysts decreased in aqueous 80 vol.% acetic acid solvent rather than in 5.7 vol.% acetic acid solvent (leaching of V: 80% in the case of V/SiO₂ catalyst in aqueous 5.7 vol.% acetic acid [8]). Particularly, the leaching of V of the V/Al₂O₃ catalyst among the investigated V catalysts was inhibited in the aqueous 80% acetic acid solvent with comparatively high yield of phenol. The stronger interaction of V species with Al₂O₃ than with SiO₂ [12] will be one of the causes for lower leaching of V on the former support. The catalytic behavior and the properties of the V/Al₂O₃ catalyst, which had a high yield of phenol and low leaching of V, for the benzene oxidation are investigated in detail hereafter.

The dependence of both the yield of phenol and the amount of accumulated H₂O₂ on the reaction time was investigated using the V/Al₂O₃ catalyst in aqueous 80 vol.% acetic acid solvent (Fig. 2). The yield of phenol increased almost linearly with the increase in the reaction time, but the degree of the increase in the yield largely retarded after the reaction time of ca. 10 h. The amount of accumulated H₂O₂ during the benzene oxidation also increased with the reaction time, but had a maximum value at the reaction time of around 20 h. The color of the reaction solution gradually changed from light-blue (V⁴⁺) at the initial reaction stage to

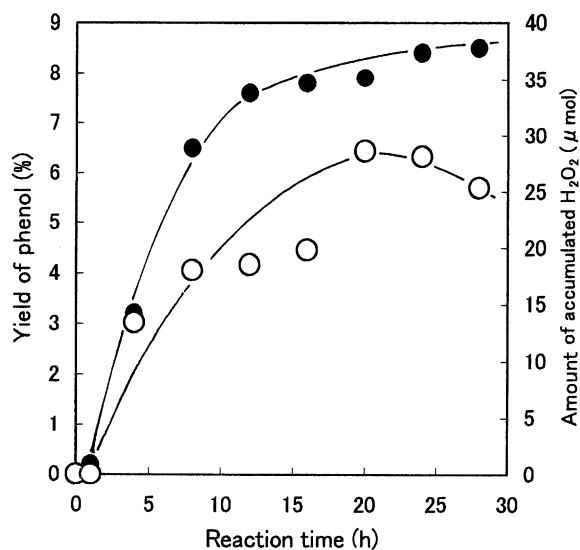


Fig. 2. Dependences of both yield of phenol and amount of accumulated H₂O₂ on reaction time. Catalyst, V/Al₂O₃ (V: 2 wt.%), 0.1 g; benzene, 5.6 mmol; solvent, 5 cm³ of aqueous solution containing 80 vol.% acetic acid; O₂, 0.4 MPa; ascorbic acid, 1 mmol; reaction temperature, 303 K; ●, yield of phenol; ○, leaching of V.

yellowish-brown (V⁵⁺) when the oxidation proceeds. The reduction of V⁵⁺ to V⁴⁺ by ascorbic acid at the initial stage, a step considered crucial for activating gaseous oxygen, may be retarded by the shortage of ascorbic acid with the progress of oxidation. Thus, the retardation of the phenol formation with the process of the oxidation may be in part due to the failure of the redox cycle of V species because of the shortage of ascorbic acid.

The influence of the partial pressure of oxygen on the yield of phenol was investigated using V/Al₂O₃ catalyst in both aqueous 80 and 5.7 vol.% acetic acid solution (Fig. 3). The phenol yield had a maximum yield at the partial pressure of oxygen of around 0.4–0.5 MPa in the case of the aqueous solvent containing 5.7 vol.% acetic acid, in agreement with our previous report [8]. The V/Al₂O₃ catalyst in the aqueous 80 vol.% acetic acid solvent gave a considerably high yield of phenol (more than 10%) at the partial pressure of O₂ at around 0.7 MPa. However, further increase in the partial pressure of O₂ tended to inversely decrease the phenol production. Thus, the higher partial pressure of O₂ was more effective for phenol formation in the case of the V-supported

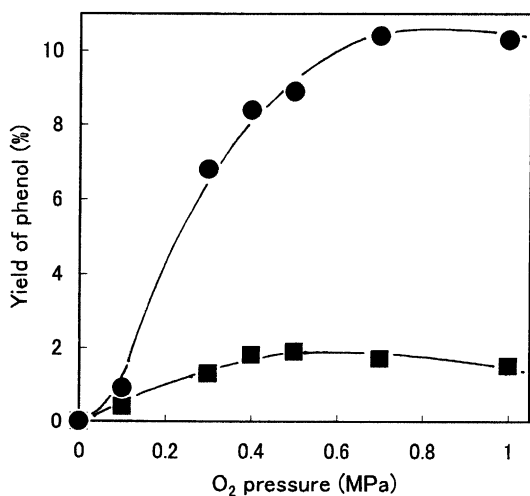


Fig. 3. Dependence of the yield of phenol on O₂ pressure. Catalyst, V/Al₂O₃ (V: 2 wt.%), 0.1 g; benzene, 5.6 mmol; ascorbic acid, 1 mmol; reaction temperature, 303 K; reaction time, 24 h; solvent: ●, 5 cm³ of aqueous solution containing 80 vol.% acetic acid; ■, 5 cm³ of aqueous solution containing 5.7 vol.% acetic acid.

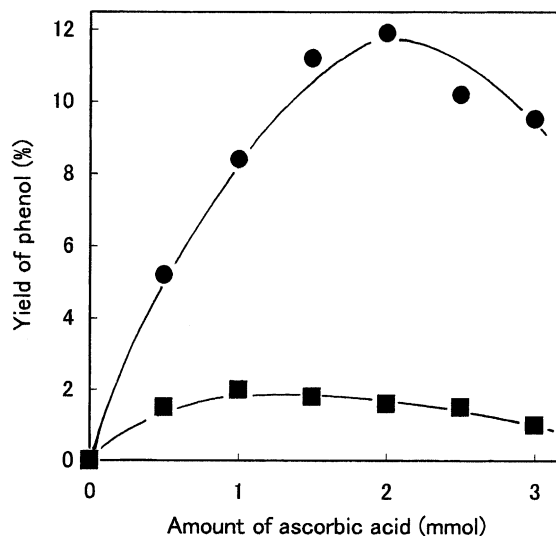


Fig. 4. Influence of the amount of ascorbic acid on the yield of phenol. Catalyst, V/Al₂O₃ (V: 2 wt.%), 0.1 g; benzene, 5.6 mmol; O₂, 0.4 MPa; reaction temperature, 303 K; reaction time, 24 h; solvent: ●, 5 cm³ of aqueous solution containing 80 vol.% acetic acid; ■, 5 cm³ of aqueous solution containing 5.7 vol.% acetic acid.

catalyst in the aqueous solvent containing 80 vol.% acetic acid. A high partial pressure of O₂ may be used to the direct oxidation of ascorbic acid presented in the reaction solution, of which the consumption of ascorbic acid may be one of the causes for the decrease in the phenol yield at a higher partial pressure of O₂.

The role of a reducing reagent was suggested [8] to activate the oxygen molecule through the reduction of the V species. Fig. 4 illustrates the dependence of the yield of phenol on the amount of ascorbic acid using aqueous solvents containing both 80 and 5.7 vol.% acetic acid. Once again, the catalytic activity of the V/Al₂O₃ for phenol formation was observed to greatly increase with the increase in the amount of ascorbic acid using the aqueous solvent containing 80 vol.% acetic acid than in the aqueous 5.7 vol.% acetic acid solvent. The yield of phenol had a maximum value at the amounts of ascorbic acid of around 2 and 1 mmol, respectively, using aqueous solvents with both 80 and 5.7 vol.% acetic acid. The presence of too much of ascorbic acid in the reaction system may in vain reduce the formed H₂O₂, a necessity for phenol formation, without utilizing for the benzene oxidation. Other reagents, including inorganic reagents, with reducing ability have been attempted in place of

ascorbic acid using the aqueous solvent containing 80 vol.% acetic acid (Table 2). Phenol was obtained using hydroquinone, pyrocatechol, or sodium sulfite as a reducing reagent, although the yield was quite lower than that by using ascorbic acid.

To investigate the effect of zinc known as a reducing reagent in acidic medium, benzene oxidation was attempted in the absence of ascorbic acid using some V-supported catalytic systems containing Zn (Table 3). No phenol was detected using a physical mixture of

Table 2
Benzene oxidation using various reducing reagents^a

Reducing reagent	Yield of phenol (%)
Ascorbic acid	8.4
Hydroquinone	1.7
Pyrocatechol	1.4
Oxalic acid	0.0
<i>i</i> -Butyl aldehyde	0.0
Sodium sulfite	0.3
Zinc acetate	0.0

^a Catalyst: V/Al₂O₃ (V: 2 wt.%), 0.1 g, benzene: 5.6 mmol; reducing reagent: 1 mmol; solvent: 5 cm³ of aqueous solution containing 80 vol.% acetic acid; O₂: 0.4 MPa; reaction temperature: 303 K; reaction time: 24 h.

Table 3
Effect of Zn as reducing reagent for the oxidation of benzene to phenol^a

Catalyst	Ascorbic acid (mmol)	Yield of phenol (%)
Zn/Al ₂ O ₃	0	0
V/Al ₂ O ₃ + Zn/Al ₂ O ₃	0	0
(Zn–V)/Al ₂ O ₃ (Zn/V = 0.5)	0	0.2
(Zn–V)/Al ₂ O ₃ (Zn/V = 20)	0	0.2
V/Al ₂ O ₃ + ZnO	0	0
V/ZnO ^b	0	0.1
V/ZnO ^c	0	0.1
V/Al ₂ O ₃	0.5	5.2
(Zn–V)/Al ₂ O ₃	0.5	6.5

^a Catalyst: 0.1 g; benzene: 5.6 mmol; solvent: 5 cm³ of aqueous solution containing 80 vol.% acetic acid; O₂: 0.4 MPa; reaction temperature: 303 K; reaction time: 24 h.

^b Prereduced at 773 K for 3 h in H₂ flow.

^c No H₂ reduction.

V/Al₂O₃ and Zn/Al₂O₃ (V/Al₂O₃+Zn/Al₂O₃). Both Zn and V co-impregnated catalyst ((Zn–V)/Al₂O₃) and V catalyst supported on ZnO (V/ZnO) had the catalytic activity for phenol formation even in the absence of ascorbic acid, although the yield of phenol was rather low. These results may suggest that the spacious closeness between V and Zn play an important role because of the easiness of the reduction of V species by the neighboring Zn. However, the increase in the amount of Zn of the ((Zn–V)/Al₂O₃) catalyst did not increase the yield of phenol. The Zn species are thus considered to be only poor reducing reagent for the present reaction in comparison with ascorbic acid. The catalytic activities of the (V–Zn)/Al₂O₃, together with the V/Al₂O₃ catalyst, for the phenol formation were also investigated in the presence of ascorbic acid (Table 3). The yield of phenol obtained using the (V–Zn)/Al₂O₃ catalyst in the presence of ascorbic acid was higher by ca. 20% than the V/Al₂O₃ catalyst. The addition of Zn to the V/Al₂O₃ catalyst was observed to promote the catalytic activity for phenol formation. This may be partly due to the reducing effect of the Zn added to the neighboring V species, though the reducing power is not so effective as described previously.

3.2. Oxidation of benzene to phenol catalyzed by V/Al₂O₃ using H₂O₂

The formation of H₂O₂ was observed during the benzene oxidation catalyzed by V/SiO₂ in the presence

of both O₂ and ascorbic acid, and the produced H₂O₂ was suggested to directly participate in the phenol formation from benzene [8]. The UV–VR spectra of the solution containing both the leached V species, obtained by allowing the V/Al₂O₃ catalyst to stand in water for 1 h, and ascorbic acid indicated the appearance of an absorption peak at ca. 200 nm, considered to be based on H₂O₂, and the decrease in the intensity of the absorption peak of ascorbic acid at 260 nm, as reported using V/SiO₂ catalyst previously [8]. The formation of H₂O₂ was thus reconfirmed using the V/Al₂O₃ catalyst in the presence of both O₂ and ascorbic acid. To investigate the behavior of H₂O₂, the liquid-phase oxidation of benzene with V/Al₂O₃ catalyst was attempted in the presence of H₂O₂ under N₂ atmosphere (0.4 MPa) in place of both O₂ and ascorbic acid. Fig. 5 illustrates the dependence of the yield of phenol on the amount of H₂O₂. The phenol yield increased with the increase in the amount of H₂O₂. However, the degree of increase in the phenol yield decreased at the H₂O₂ amounts of more than around 6 mmol, which is approximately similar to the initial amount of benzene (5.6 mmol). This may indicate that the amounts of H₂O₂ more than the initial amount of benzene will self-decompose and will not be effectively utilized for phenol formation.

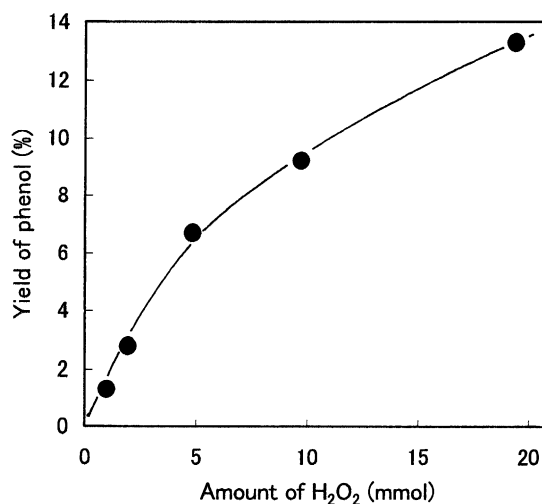


Fig. 5. Benzene oxidation catalyzed by V/Al₂O₃ using H₂O₂ oxidant. Catalyst, V/Al₂O₃ (V: 2 wt.%), 0.1 g; benzene, 5.6 mmol; 5 cm³ of aqueous solution containing 80 vol.% acetic acid; N₂, 0.4 MPa; reaction temperature, 303 K; reaction time, 24 h; solvent.

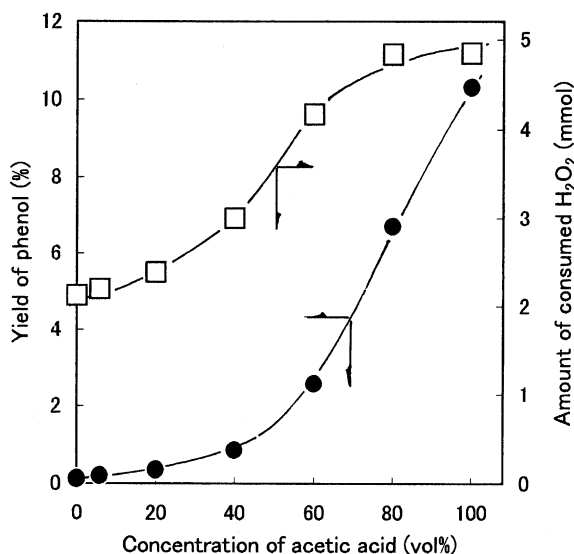


Fig. 6. Influence of concentration of acetic acid on both the yield of phenol (●) and the amount of consumed H₂O₂ (□) in the benzene oxidation using H₂O₂. Catalyst, V/Al₂O₃ (V: 2 wt.%), 0.1 g; benzene, 5.6 mmol; H₂O₂, 4.85 mmol; 5 cm³ of aqueous solution containing acetic acid; N₂, 0.4 MPa; reaction temperature, 303 K; reaction time, 24 h; solvent.

H₂O₂ has been reported [13] to be more stable in acidic medium and to inhibit the self-decomposition. The dependence of the volumetric concentration of acetic acid in the aqueous solvent on both the yield of phenol and the amount of H₂O₂ consumption was investigated using the V/Al₂O₃ catalyst and H₂O₂ (Fig. 6). The amount of H₂O₂ consumption was estimated by deducting the amount of H₂O₂ that remained in the reaction solution from the amount of fed H₂O₂. The yield of phenol increased continuously with the increase in the volumetric concentration of acetic acid in the aqueous solvent; it increased even more sharply at the acetic acid concentrations of more than ca. 50 vol.%. The similar dependence between the yield of phenol and the concentration of acetic acid, except the region of the concentrations of acetic acid of more than around 80 vol.% was observed using both gaseous O₂ and ascorbic acid (Figs. 1A and B). The amount of consumed H₂O₂, together with the yield of phenol, was also increased with increasing the concentration of acetic acid. This may suggest that the H₂O₂ in the aqueous solvent containing higher concentrations of acetic acid is utilized

efficiently for the formation of phenol. The discrepancy between gaseous O₂ as an oxidant and ascorbic acid as a reducing reagent, and H₂O₂ was clearly shown at the acetic acid concentrations of more than ca. 80 vol.%. The formation of H₂O₂, which is prerequisite for phenol formation, using the supported V catalyst in the presence of both O₂ and ascorbic acid may necessitate the participation of water although we have no experimental evidence on this matter.

3.3. Inhibition effect of added alcohol in the oxidation of benzene to phenol

The effect of alcohol, which is well known as a scavenger for the hydroxy radical, added to the reaction system on the yield of phenol was investigated using the V/Al₂O₃ catalyst in the aqueous solvent containing 80 vol.% acetic acid to confirm the participation of the hydroxyl radical assumed to be formed by the decomposition of H₂O₂ during the benzene oxidation. If the hydroxy radical produced during the benzene oxidation is assumed to react with both benzene and added alcohol, the concentrations of the formed phenol and the added alcohol will be related according to following equation, in the simplest form [7]:

$$\frac{[\text{Phenol}]_0}{[\text{Phenol}]} \approx 1 + \frac{k_2[\text{Benzene}]}{k_1}[\text{Alcohol}]$$

where [Phenol]₀ and [Phenol] are concentrations of phenol produced without and with the added alcohol, respectively. [Benzene] and [Alcohol] are concentrations of benzene and the added alcohol (these concentrations are assumed to be approximately constant). k_1 and k_2 are the rate constants of the reactions between benzene and the hydroxy radical, and between alcohol and the hydroxy radical, respectively. The plot between [Phenol]₀/[Phenol] and [Alcohol] is illustrated in Fig. 7 using both ethanol and methanol as an added alcohol. The plot was almost linear, regardless of the added alcohol. The direct participation of hydroxy radical during the oxidation of benzene also using the V/Al₂O₃ catalyst was suggested as reported previously using Cu/MCM-41 catalyst [7]. The added ethanol increased the phenol yield higher than the added methanol did. The result of Fig. 7 is consistent with the higher ability of ethanol for scavenging hydroxy radical than that of methanol.

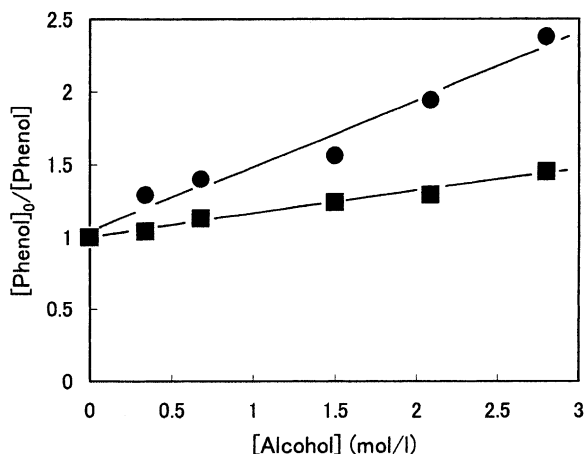


Fig. 7. Influence of addition of alcohol on the yield of phenol. Catalyst, V/Al₂O₃ (V: 2 wt.%), 0.1 g; benzene, 5.6 mmol; solvent, 5 cm³ of aqueous solution containing 80 vol.% acetic acid; O₂, 0.4 MPa; ascorbic acid, 1 mmol; reaction temperature, 303 K; ●, ethanol addition; ■, methanol addition.

4. Conclusions

The volumetric concentration of acetic acid in the aqueous solvent was found to greatly influence to the catalytic activity of the supported V catalysts for the phenol formation in the liquid-phase oxidation of benzene in the presence of gaseous oxygen as an oxidant and ascorbic acid as a reducing reagent. The V-supported oxide catalysts, such as V/SiO₂ and V/Al₂O₃, gave a maximum yield of phenol in the aqueous solvent containing around 80 vol.% acetic acid. The yield of phenol catalyzed by the V/Al₂O₃ using H₂O₂, in place of both gaseous O₂ and ascorbic acid, also increased with the increase in the volumetric concentration of acetic acid in the aqueous solvent, as observed by the corresponding catalyst using both O₂ and ascorbic acid, except the region of the acetic acid concentrations of more than ca. 80 vol.%. The amount of H₂O₂ consumed during the benzene oxidation also increased with the increase in the volumetric concentration of acetic acid of the aqueous solvent. The effective utilization to phenol formation of H₂O₂

formed catalyzed by V/Al₂O₃ in the presence of both O₂ and ascorbic acid was suggested to be one of the reasons of highest yield of phenol in the aqueous solvent containing 80 vol.% acetic acid, although it is not clearly understandable, from the current report, why the yield of phenol decreases at the volumetric concentration of acetic acid of more than ca. 80 vol.%. The direct participation of the hydroxy radical, which will be formed from the decomposition of produced H₂O₂, was suggested based on the inhibition effect for phenol formation of added alcohol.

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