Liquid-phase oxygenation of benzene over supported vanadium catalysts

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The liquid-phase oxygenation of benzene was studied using supported vanadium(V) catalysts. Molecular oxygen and ascorbic acid were used as the oxidant and reducing reagent, respectively. The reduced vanadium species is suggested to be the active catalytic species in this reaction system. The catalytic activity of the supported V catalysts for phenol formation was found to be somewhat higher than those of supported Cu counterparts. The addition of Cu ions to the supported V catalyst caused an increase in the yield of phenol. The leaching of the catalytically active V species from the support during the liquid-phase oxidation was also inhibited by the addition of Cu ions to the supported V catalysts. The concentration of acetic acid in the aqueous solvent was found to have an optimum value for the phenol production. The formation of hydrogen peroxide was observed during the benzene oxidation catalyzed by the supported V catalyst, and the accumulated amount of the formed hydrogen peroxide was quantitatively detected by iodometry. The electronic absorption spectra of the reaction solution including the V species also indicated the formation of hydrogen peroxide during the benzene oxidation. The produced hydrogen peroxide was suggested to directly participate in the phenol formation from benzene.

Introduction

Phenol, a precursor for important synthetic chemicals such as phenol resin, bisphenol A, and caprolactam, has been manufactured mainly by the cumene method, which is characterized by a multistep process and the production of acetone as a byproduct. The development of phenol production by a one-step process will have advantages economically and/or energetically. In the 1960s, Norman and coworkers[1] studied a one-step benzene oxidation to form phenol using a ferric sulfate–H_2O_2 system (Fenton's reagent). More recently, liquid-phase benzene oxidation with oxygen as oxidant, in place of hydrogen peroxide which is more expensive and harder to use, in the presence of a reductant has been reported using catalytic systems containing transition metal ions such as copper ions.[2–4] Other interesting liquid-phase oxidations of benzene to phenol have been reported, for example, a liquid-phase cooxidation method[5,6] in which benzene was oxidized by a corresponding peracid formed by acetaldehyde and oxygen, *sec*-butylbenzene oxidation to form phenol and methyl ethyl ketone,[5,6] and a liquid-phase benzene oxidation catalyzed by a heteropolyacid–triphenylphosphine system.[7,8] We have been studying a one-step formation of phenol by benzene oxidation using copper catalysts supported on oxides including zeolites and oxygen as oxidant, in which ascorbic acid has been used as a reductant for the copper species.[9] Also, copper ion-exchanged and/or impregnated MCM-41 has been reported to be a catalyst for phenol formation by liquid-phase catalyzed benzene oxidation.[10]

In this study, liquid-phase catalytic benzene oxidation has been attempted under a variety of reaction conditions using supported vanadium catalysts, molecular oxygen as oxidant, and ascorbic acid as a reductant. H_2O_2 accumulated during the benzene oxidation catalyzed by the supported vanadium was quantitatively analyzed. The redox behavior of the vanadium species was investigated by electronic absorption spectra of the homogeneous vanadium catalysts during the benzene oxidation. A scheme for phenol formation was elucidated based on the data for the accumulated H_2O_2 and the variation in the electronic absorption spectra during the benzene oxidation, in addition to the results of the oxidation reaction.

Experimental

Catalyst preparation

SiO_2 (JRC-SIO-8), TiO_2 (JRC-TIO-2, JRC-TIO-5), Al_2O_3 (JRC-ALO-4) and mordenite (JRC-Z-M20, Si/Al = 10) were obtained from the Japan Catalysis Society. MgO (Nacalai Tesque, guaranteed reagent), NaX (Toso, Zeolem F-9, Si/Al atomic ratio = 2.4), NaY (Toso, Si/Al = 2.8) and KL (Toso, Si/Al = 3.4) were obtained commercially. NaZSM-5 (Si/Al = 43) was synthesized according to the patent.[11] MCM-41 (BET surface area = 1052 $m^2\ g^{-1}$) was synthesized according to the literature.[10] All the supported vanadium catalysts were prepared by an impregnation method using a prescribed concentration of aqueous $VO(acac)_2$ [bis(acetylacetonato)oxovanadium, Nacalai Tesque, guaranteed reagent] solution, in which solution a small amount of citric acid (Nacalai Tesque, extra pure reagent) was added to make the aqueous solution completely homogeneous. After evaporation of water, all the vanadium-impregnated catalysts were dried at 393 K overnight and calcined at 573 K for 3 h in flowing air (206 $cm^3\ min^{-1}$). The Cu and V co-impregnated SiO_2 [(Cu-V)/SiO_2] catalyst was prepared using a homogeneous aqueous solution including the prescribed concentrations of both $Cu(AcO)_2 \cdot H_2O$ (Nacalai Tesque, guaranteed reagent) and $VO(acac)_2$. The resulting (Cu-V)/SiO_2 was dried at 393 K overnight and calcined at 573 K for 3 h in flowing air. The quantitative analyses of V and Cu species were performed using a Shimazu Model AA-630-01 atomic absorption spectrophotometer.

Liquid-phase catalytic oxidation of benzene

Benzene (Nacalai Tesque, guaranteed reagent) was purchased commercially and used without further purification after an impurity check using GLC. Ascorbic acid (guaranteed reagent) and 1 M aqueous acetic acid solution (guaranteed reagent) were obtained from Nacalai Tesque Co. A high pressure stainless steel reactor (Taiatsu Glass Co.) was used when the benzene oxidation was operated under oxygen atmosphere of more than 1 atm. The catalyst (0.1 g), 5 cm^3 of 1 M aqueous acetic acid solvent, 0.5 cm^3 of benzene (5.6 mmol), and ascorbic acid (1 mmol) were added into the reactor and stirred by a magnetic stirrer at 333 K for 24 h under 0.4 MPa of oxygen. The benzene oxidation under atmospheric oxygen was performed by adding 0.4 g of catalyst, 20 cm^3 of 1 M aqueous acetic acid solvent, 2 cm^3 of benzene (22.5 mmol), and ascorbic acid (4 mmol) into a 50 cm^3 glass flask and stirring the whole reaction system magnetically. After the reaction, a prescribed amount of propan-2-ol, as an internal standard, was added to the reaction mixture. The reaction solution containing added propan-2-ol was centrifuged to completely precipitate the solid catalyst and analyzed by GLC (Shimazu Model GC-8A) using a 3 m stainless steel column containing Silicon OV-17 and/or a 1.5 m stainless steel column containing Thermon-3000 5% on Shincarbon A at 453 and 493 K, respectively, with a N_2 gas carrier (44 cm^3 min^{-1}).

Quantitative analysis of H_2O_2 accumulated during the benzene oxidation by supported vanadium catalysts

After benzene oxidation for the prescribed time and separation of the solid catalyst from the heterogeneous reaction system by centrifugation, the amount of H_2O_2 in the reaction solution was quantitatively analyzed by iodometry. Small amounts of sodium hydrogen carbonate were added to prevent the autoxidation of I^- ions, and the analyses were quickly performed in the dark.

Electronic absorption spectra of V species and H_2O_2 in the reaction solution

The electronic absorption spectra of V species and H_2O_2 in the reaction solution were measured at room temperature by a Shimazu Model UV-240 spectrophotometer.

DTA-TG measurement of uncalcined V/SiO_2

The differential thermal and thermogravimetric analyses (DTA-TG) of the uncalcined V/SiO_2 catalyst, which was only dried at 393 K overnight, were conducted in the region of 293–773 K under flowing air (30 cm^3 min^{-1}) at a programmed rate of 20 K min^{-1} using SiO_2 (JRC-SIO-8) as standard.

Results

Liquid-phase catalytic oxidation of benzene

The oxidation product obtained was phenol. A trace of biphenyl was detected under some reaction conditions. Fig. 1 illustrates the results of the liquid-phase benzene oxidation catalyzed by the supported V catalysts under atmospheric oxygen and 0.4 MPa pressure. The results obtained with the supported Cu catalysts, the supported Cu systems which have already been reported,[9,10] are also shown in Fig. 1 to compare the activities for phenol formation of both catalysts. The activities of the Cu catalysts (Cu/SiO_2, Cu/NaY) supported on SiO_2 and NaY for phenol formation hardly varied with an increase in the oxygen pressure. In contrast to the supported Cu catalysts, the phenol yields catalyzed by V catalysts (V/SiO_2, V/NaY) supported on SiO_2 and NaY increased with an increase in the oxygen pressure; in particular, the V/SiO_2 catalyst showed high activity for phenol formation under an oxygen atmosphere of 0.4 MPa.

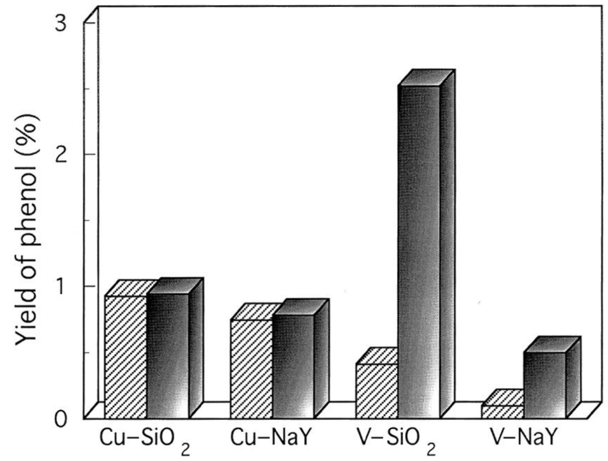


Fig. 1 Benzene oxidation catalyzed by supported Cu and V catalysts. Catalyst, 0.1 g (Cu, V; 2.0 wt% except Cu-NaY (Cu; 3.3 wt%)); reaction time, 24 h; reaction temperature, 303 K; (▨), 0.1 MPa; (■), 0.4 MPa.

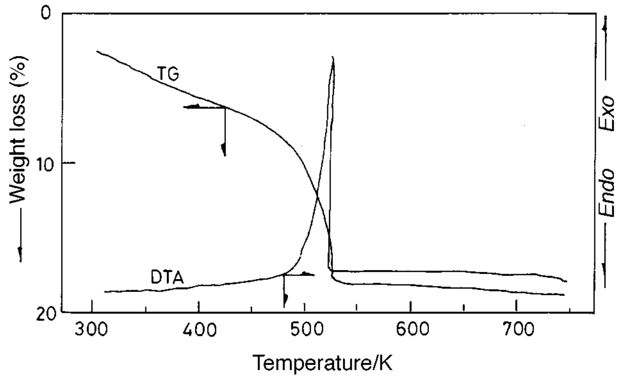


Fig. 2 DTA-TG curves of V/SiO_2 catalyst. Catalyst, uncalcined V/SiO_2 (V; 10 wt%); heating rate, 20 K min^{-1}; reference sample, SiO_2.

The DTA-TG profiles of dried V/SiO_2 prepared using $VO(acac)_2$ as a vanadium salt precursor were measured, as illustrated in Fig. 2. A large sharp exothermic peak was observed at around 513–533 K together with a weight loss. The exothermic peak is considered to be due to the combustion of the organic ligands of the vanadium salt.[12] All V/SiO_2 catalysts were calcined at 573 K for 3 h in flowing air before using them for benzene oxidation. V/SiO_2 catalysts prepared using different vanadium salts were tried as catalysts for liquid-phase benzene oxidation (Fig. 3). The difference between the catalytic activities for phenol formation of these catalysts was not particularly large under the present reaction conditions, although the V/SiO_2 catalyst prepared from $VO(acac)_2$ had the highest activity.

The influence of the support for the V species using $VO(acac)_2$ as a precursor on the activity for phenol formation is shown in Table 1. The structure of the supported vanadium species has been reported[13,14] to be greatly influenced by the supports used. An inert support such as SiO_2 was found to be more effective than supports which have a comparatively strong interaction with vanadium oxides, such as TiO_2. The higher the Si/Al atomic ratios of the zeolite supports, the higher the yields of phenol tended to be. The high hydrophobicity of the zeolites with higher Si/Al atomic ratios may facilitate the access of benzene molecules into the micropores.

The influence of leaching of the V species from the V/SiO_2 catalyst into the reaction solution on the yield of phenol was

Table 1 Effect of support on yield of phenol[a]

Support	BET surface area/m^2 g^{-1}	Si/Al atomic ratio	Yield of phenol (%)
SiO_2	303	—	2.5
TiO_2 (anatase)	18	—	1.1
TiO_2 (rutile)	3	—	0.4
Al_2O_3	177	—	1.5
MgO	6	—	0.1
MCM-41[b]	1052	31	1.1
NaX	555	2.4	0.6
NaY	870	2.8	0.5
KL	323	3.4	1.4
Mordenite	399	10	1.6
NaZSM-5	355	43	1.9

[a] Catalyst: V supported catalyst (V, 2.0 wt%), 0.1 g; solvent: 1 M acetic acid, 5 cm^3; reducing agent: ascorbic acid, 1 mol; reaction time: 24 h; reaction temperature: 303 K; O_2 pressure: 0.4 MPa. [b] Pore size: 31 Å.

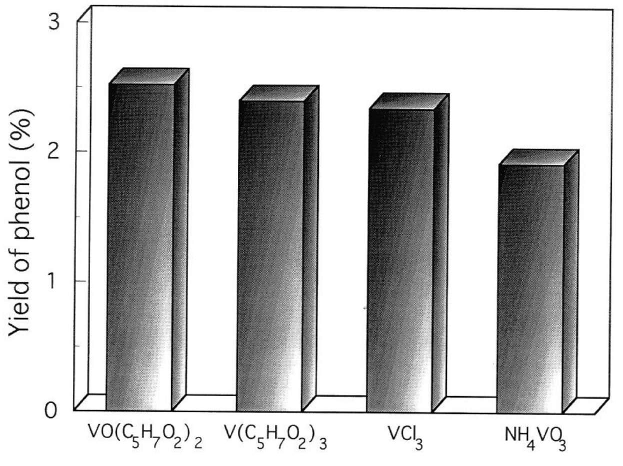


Fig. 3 Influence of vanadium salt as a precursor for V/SiO_2 catalyst on phenol yield. Catalyst, V/SiO_2, 0.1 g (amount of V; 2 wt%); reaction pressure, 0.4 MPa O_2; reaction temperature, 303 K; reaction time, 24 h.

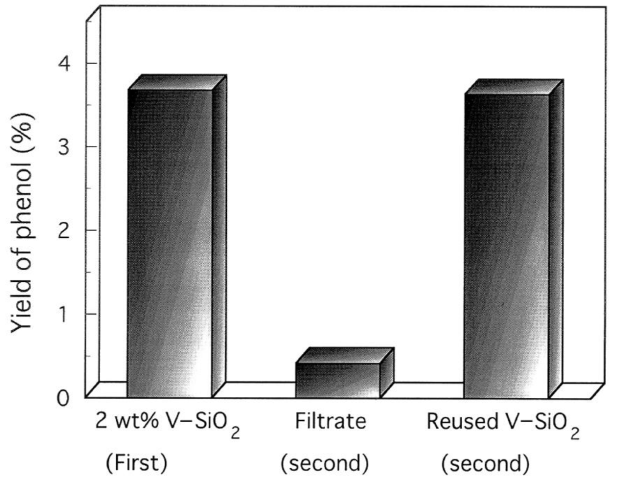


Fig. 4 Benzene oxidation by used V/SiO_2 catalyst and the filtrate. Catalyst, V(2)/SiO_2, 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reductant, ascorbic acid, 1 mmol; reaction time, 24 h; reaction temperature, 333 K.

Table 2 Benzene oxidation catalyzed by fresh and used catalysts[a]

Run	Yield of phenol (%)	Leaching of V (%)
1 (fresh catalyst)	3.7	80.0
2 (first used catalyst)	3.5	92.3
3 (second used catalyst)	2.0	97.8
4 (third used catalyst)	1.2	97.9

[a] Catalyst: V/SiO_2 (fresh catalyst, V = 2.0 wt%), 0.1 g; solvent: 5 cm^3 of 1 M acetic acid; reducing agent: 1 mmol of ascorbic acid; reaction temperature: 333 K; reaction time: 24 h; O_2 pressure: 0.4 MPa.

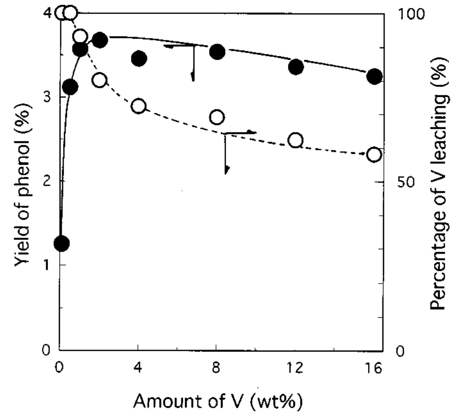


Fig. 5 Influence of amount of V on the yield of phenol. Catalyst, V/SiO_2, 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reductant, ascorbic acid, 1 mmol; reaction time, 24 h; reaction temperature, 333 K; (●), yield of phenol; (○), percentage of leaching V.

investigated using the filtrate and the used catalyst, respectively, separated by centrifugation after the first benzene oxidation (Fig. 4). The percentage of leaching of V species after the first benzene oxidation catalyzed by a fresh 2 wt% vanadium supported SiO_2 catalyst (V(2)/SiO_2) was 80%. A small amount of phenol was produced by the benzene oxidation in the filtrate. It is of interest to note that the used V/SiO_2 catalyst, from which the amount of the supported V species had decreased by 80%, had a catalytic activity for benzene formation similar to that of the fresh V(2)/SiO_2 catalyst. The results of repeated catalyst reuse are given in Table 2. As is shown, the yield of phenol decreased gradually with repeated catalyst reuse. The percentage of leaching of V species was highest in the case of the fresh V/SiO_2 catalyst (run 1). It must be noted that the used V/SiO_2 catalysts with percentages of V leaching of more than 97% showed phenol yields of 2.0–1.2% (runs 3 and 4). All of the phenol yields in this study were evaluated as total yields catalyzed by both the heterogeneous V/SiO_2 and the filtrate.

The influence of the amount of V species supported on the V/SiO_2 catalyst on the yield of phenol is illustrated in Fig. 5. The phenol yield sharply increased with the increase in the supported V species up to a V supported amount of around 1 wt%, had a maximum value at a supported V of *ca.* 2 wt%, and tended to decrease with a supported V species of more than 2 wt%. The percentage of leaching of the V species after 20 h reaction, which is also illustrated in Fig. 5, tended to decrease with the amount of supported V.

The Cu-V co-impregnated SiO_2 catalysts, in which the content of Cu was constant at 2 wt% and the V content was varied, were tested as catalysts for benzene oxidation to investigate the effect of the co-existing Cu species (Fig. 6). The yields of phenol catalyzed by Cu-V/SiO_2 (Fig. 6) were higher than those by the V/SiO_2 catalysts (Fig. 5). Also the leaching of both V and Cu species was found to be greatly inhibited in the V and Cu co-existing system.

Fig. 7 illustrates the time dependence of the yield of phenol at both 303 and 333 K. The yields of phenol at both reaction temperatures increased with time until a reaction time of around 10 h, but the extent of increase in the phenol yield with the reaction time sharply decreased at a reaction time of more than 10 h. This is due to the deactivation of the V/SiO_2 catalyst and/or the self-oxidation of ascorbic acid added as a reductant during the prolonged reaction.

The influence of reaction temperature on the phenol yield was investigated using a V(2)/SiO_2 catalyst (Fig. 8). The phenol

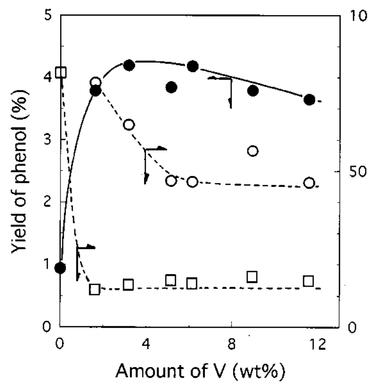


Fig. 6 Benzene oxidation by (Cu-V)/SiO$_2$ catalyst. Catalyst, Cu-V/SiO$_2$ (Cu; 2 wt%), 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reductant, ascorbic acid, 1 mmol; reaction time, 24 h; reaction temperature, 333 K; O$_2$ pressure, 0.4 MPa; (●), yield of phenol; (○), percentage of leached V; (□), percentage of leached Cu.

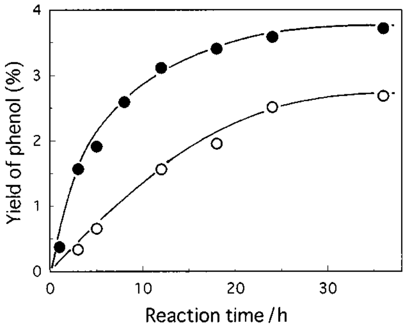


Fig. 7 Plots of the yield of phenol *vs.* reaction time. Catalyst, V(2)/SiO$_2$, 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reductant, ascorbic acid, 1 mmol; O$_2$ pressure, 0.4 MPa; reaction temperature, (●) 333 K, (○) 303 K.

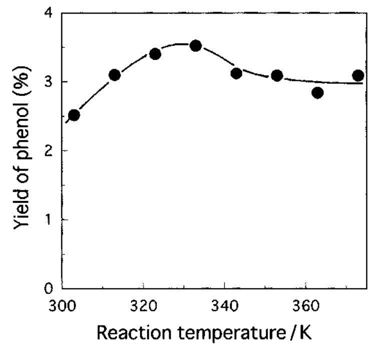


Fig. 8 Influence of reaction temperature on the yield of phenol. Catalyst, V(2)/SiO$_2$, 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reductant, ascorbic acid, 1 mmol; O$_2$ pressure, 0.4 MPa; reaction time, 24 h.

Table 3 Influence of reductant on the yield of phenol[a]

Reductant	Amount/ mmol	Yield of phenol (%)
Hydroquinone	0.1	0.4
	0.5	1.4
	1.0	1.1
Pyrocatechol	0.1	0.9
	0.5	2.1
	1.0	1.8

[a] Catalyst: V(2)/SiO$_2$ (V, 2.0 wt%), 0.1 g; solvent: 1 M acetic acid, 5 cm^3; reaction time: 24 h; reaction temperature: 333 K; atmosphere: 0.4 MPa of O$_2$.

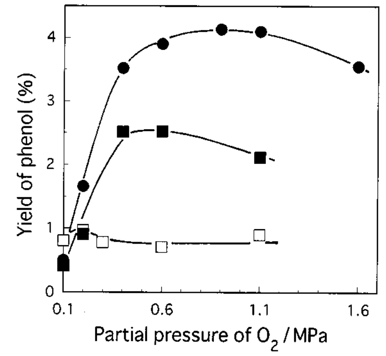


Fig. 9 Influence of O$_2$ pressure on the yield of phenol. Catalyst, V(2)/SiO$_2$, Cu(3.3)/NaY, 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reductant, ascorbic acid, 1 mmol; reaction time, 24 h; (■), V(2)/SiO$_2$, reaction temperature, 303 K; (●), V(2)/SiO$_2$, reaction temperature, 333 K; (□), Cu(3.3)/NaY, reaction temperature, 303 K.

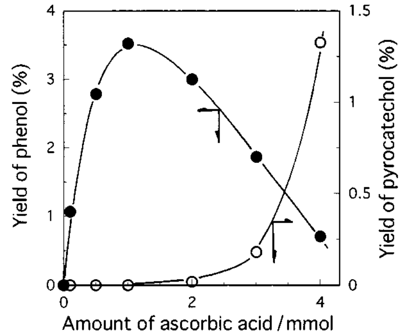


Fig. 10 Influence of amount of ascorbic acid on the yield of phenol. Catalyst, V(2)/SiO$_2$, 0.1 g; solvent, aqueous 1 M acetic acid, 5 cm^3; reaction time, 24 h; reaction temperature, 333 K; (●), yield of phenol; (○) yield of pyrocatechol.

yield gradually increased with reaction temperature up to 333 K but a further increase in the temperature caused a decrease in the phenol yield, and a maximum value was reached at a reaction temperature of around 333 K. The turnover numbers in Fig. 8, defined as 'produced phenol/(total V species in both V/SiO$_2$ and the reaction solution)' (mole ratio), had values of 3.8–5.1.

The dependence on oxygen pressure of the phenol yields catalyzed by both V(2)/SiO$_2$ and Cu(3.3)/NaY catalysts is illustrated in Fig. 9. Both catalysts had no catalytic activity for phenol formation under a nitrogen atmosphere. The phenol yields catalyzed by Cu(3.3)/NaY did not have a high dependence on oxygen pressure and were almost constant at *ca.* 1%, regardless of any variation in the oxygen pressure. On the contrary, the yield of phenol catalyzed by V(2)/SiO$_2$ at a reaction temperature of 303 K increased with the increase in oxygen pressure up to around 0.4 Pa, although a further increase in the oxygen pressure caused a slight decrease in phenol yield. The extent of increase in phenol yield with oxygen pressure was higher at higher reaction temperatures.

The influence of the amount of reductant, ascorbic acid, on the yield of phenol was investigated under a constant oxygen pressure using a V(2)/SiO$_2$ catalyst (Fig. 10). The SiO$_2$-supported vanadium catalyst had no catalytic activity for phenol formation in the absence of ascorbic acid. The phenol yield greatly increased with the increase in the amount of ascorbic acid up to 1 mmol, but further addition of ascorbic acid caused a sharp decrease in the phenol yield and formation of pyrocatechol. Pyrocatechol is considered to be produced as a consequence of further hydroxylation of phenol because pyrocatechol appeared together with a decrease in the yield of phenol. Table 3 shows the results of benzene oxidation using both catechol and hydroquinone as the reducing reagent, in place of ascorbic acid. Both catechol and hydroquinone were

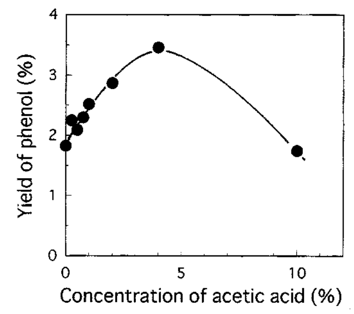


Fig. 11 Influence of concentration of acetic acid on the yield of phenol. Catalyst, V(2)/SiO$_2$, 0.1 g; reductant, ascorbic acid, 1 mmol; reaction time, 24 h; reaction temperature, 303 K.

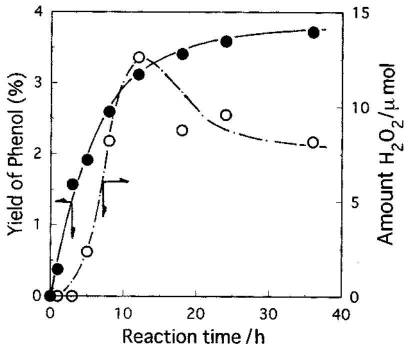


Fig. 12 Plots of yield of phenol and accumulated H$_2$O$_2$ amount *vs.* reaction time. Catalyst, V(2)/SiO$_2$, 0.1 g; reductant, ascorbic acid, 1 mmol; solvent, aqueous 1 M acetic acid, 5 cm^3; reaction temperature, 333 K; (●), yield of phenol; (○), amount of accumulated H$_2$O$_2$.

Table 4 Influence of reductant and O$_2$ on the yield of phenol[a]

Catalyst	Ascorbic acid/ mmol	Atmosphere (0.4 MPa)	Yield of phenol (%)
V/SiO$_2$	0	N$_2$	0
	0	O$_2$	0
	1	N$_2$	0
	1	O$_2$	3.7
Cu-V/SiO$_2$	0	N$_2$	0
	0	O$_2$	0
	1	N$_2$	0
	1	O$_2$	4.2

[a] Catalyst: V(2)/SiO$_2$ (V, 2.0 wt%), 0.1 g: Cu-V/SiO$_2$ (V/Cu atomic ratio = 2, Cu = 2.0 wt%), 0.1 g; solvent: 1 M acetic acid, 5 cm^3; reaction time: 24 h; reaction temperature: 333 K.

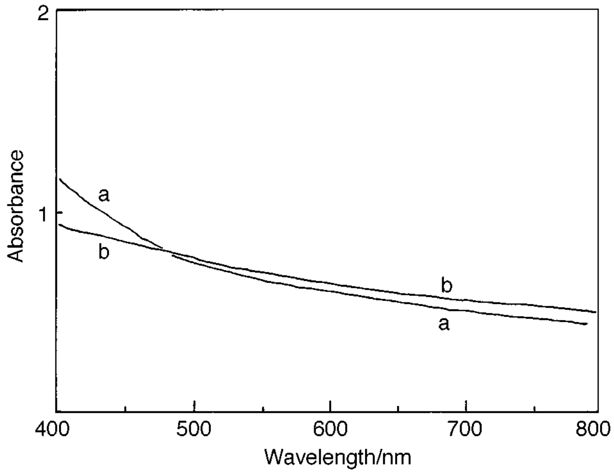


Fig. 13 Visible light spectra of V species leached into water from V/SiO$_2$. Concentration of leached V species, 1.1 × 10^{-3} mol dm^{-3}; added ascorbic acid, 3.2 × 10^{-7} mol; (a), V species; (b), V species + ascorbic acid.

found to function as effective reducing reagents for the V/SiO$_2$ catalyst although the yields of phenol were not very high.

The effect of the concentration of acetic acid in the aqueous solvent on the yield of phenol using the V(2)/SiO$_2$ catalyst at 303 K is illustrated in Fig. 11. A 1.8% phenol yield was obtained even without acetic acid (water solvent). The phenol yield increased with the increase in the acetic acid concentration and passed through a maximum value at a concentration of around 4 mol dm^{-3}.

Formation and accumulation of hydrogen peroxide during benzene oxidation catalyzed by V/SiO$_2$

The present V/SiO$_2$ catalytic system using molecular oxygen as an oxidant and ascorbic acid as a reductant is considered to proceed *via* a reaction scheme similar to a Fenton-type reaction;[1,15] therefore, the amount of hydrogen peroxide that accumulated during benzene oxidation was quantitatively measured, together with the results of the phenol yield, as illustrated in Fig. 12. The amount of accumulated H$_2$O$_2$ sharply increased with reaction time and passed through a maximum value at around 12 h. The yield of phenol also greatly increased with reaction time, but the extent of the increase in the phenol yield decreased beyond a reaction time of *ca.* 12 h. The intermediate H$_2$O$_2$ formed during benzene oxidation is suggested to play an important role in phenol production as seen in a Fenton-type reaction scheme.

Electronic absorption spectra of V species in the reaction solution

The aqueous V species leached from the V/SiO$_2$ catalyst which was placed in ion-exchanged water were observed at room temperature *via* their electronic absorption spectra in the wavelength region of 400–800 nm (Fig. 13). The addition of ascorbic acid to the aqueous solution of the leached V species caused a decrease in the absorbance at 460–490 nm and an increase in the absorbance at 570–580 nm. This observation is consistent with the color change in the aqueous solution from yellow to pale blue on adding ascorbic acid. The process of H$_2$O$_2$ formation in an aqueous solution including leached V species and ascorbic acid was followed by electronic absorption spectroscopy (Fig. 14). The spectrum of the aqueous solution including both leached V species and ascorbic acid changed from Fig. 14A-a (initial stage) to Fig. 14A-b (after standing for 1 h in the atmosphere). The electronic absorption spectra of an aqueous solution including the leached V, ascorbic acid and H$_2$O$_2$ (Fig. 14A-c), an aqueous H$_2$O$_2$ solution (Fig. 14B-d), an aqueous ascorbic acid solution (Fig. 14B-e), and the aqueous ascorbic acid solution left for 1 h in the atmosphere (Fig. 14B-f) were also measured as references. The absorption peak at 215 nm based on H$_2$O$_2$[16] was not observed at the initial stage of mixing of V species and ascorbic acid (Fig. 14A-a) but clearly appeared on exposure of the solution to the air (Fig. 14A-b), and the spectrum of Fig. 14A-b was almost superimposed over the spectrum (Fig. 14A-c) of the aqueous solution including H$_2$O$_2$. The standing of aqueous ascorbic solution without V species for 1 h in air did not give an absorption peak at 215 nm and only decreased the peak based on ascorbic acid. (Fig. 14B-e→ Fig. 14B-f). The formation of H$_2$O$_2$ from an aqueous solution including V species, ascorbic acid, and O$_2$ was thus confirmed by the electronic absorption spectra.

Discussion

No phenol was produced in the benzene oxidation using a V/SiO$_2$ or Cu-V/SiO$_2$ catalyst in the absence of both ascorbic acid and O$_2$ (Table 4). Both an oxidant and a reductant were thus found to be necessary for the formation of phenol by benzene oxidation over the V/SiO$_2$ or (Cu-V)/SiO$_2$ catalysts. As

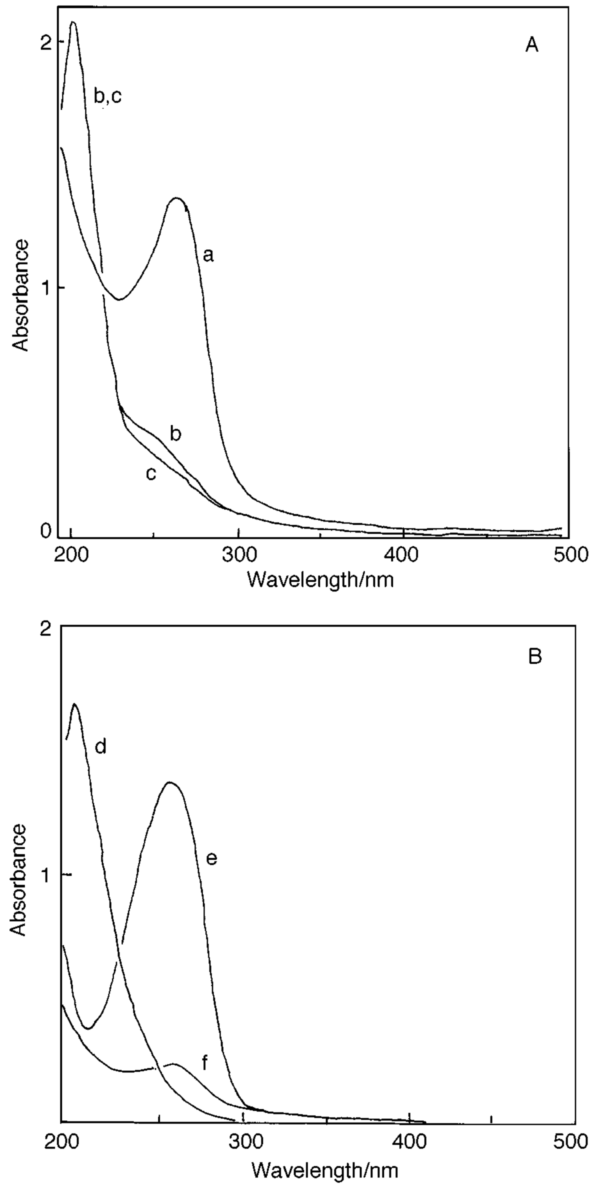
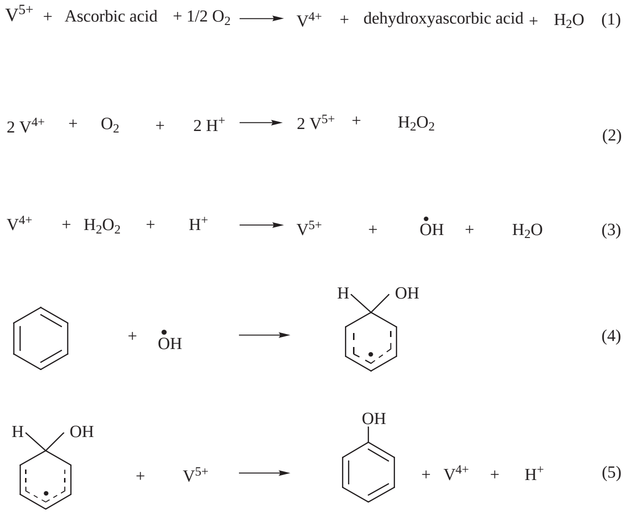


Fig. 14 UV-VIS spectra of leached V species. Concentration of V, 1.1×10^{-4} mol dm^{-3}; added ascorbic acid, 3.2×10^{-7} mol; added H_2O_2, 1.6×10^{-7} mol; A: (a) V species + ascorbic acid (initial stage), (b) V species + ascorbic acid (after 1 h in air), (c) V species + ascorbic acid + H_2O_2; B: (d) H_2O_2, (e) ascorbic acid (immediately after the addition of ascorbic acid), (f) ascorbic acid (after 1 h in air).

a reductant, in addition to ascorbic acid, hydroquinone or pyrocatechol[17] were also effective for the phenol formation although the yield of phenol was not as high as with ascorbic acid because of the self-oxidation of the corresponding quinone or catechol with oxygen (Table 3).

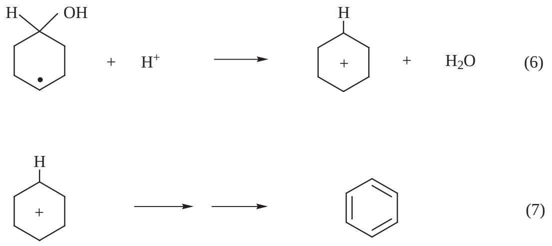
Although the yields of phenol catalyzed by (Cu-V)/SiO_2 were slightly higher than those by a V/SiO_2 catalyst, the influence of the Cu species added to the V/SiO_2 catalyst on phenol formation is not great, as evidenced by a comparison of Figs. 5 and 6. However, the leaching of V species from the Cu-V/SiO_2 catalyst (Fig. 6) was found to be inhibited in comparison with the V/SiO_2 counterpart (Fig. 5). As one of the methods of prohibiting the leaching of the supported V species, the impregnation of a second component such as Cu species in the V/SiO_2 catalyst may be effective, although we do not know the reason at the present stage.

The formation of H_2O_2 was directly observed *via* electronic absorption spectroscopy of the aqueous solution including both V species leached from the V/SiO_2 catalyst and ascorbic acid in air (Fig. 14). H_2O_2 was found to be formed only in the presence of the three components, the V species, ascorbic acid (reductant), and O_2 (oxidant). The yield of phenol increased with the increase in the accumulated H_2O_2 at the initial stage of benzene oxidation catalyzed by V/SiO_2, and a decrease in the accumulated H_2O_2 caused a considerable decrease in the rate of phenol formation (Fig. 12). The decrease in the rate of phenol formation may be in part caused by the deactivation of the catalyst during the benzene oxidation. Also the decrease in the accumulated H_2O_2 during the oxidation will be due in part to the self-decomposition of H_2O_2 without direct participation in the benzene oxidation. Although a direct correlation between the rate of phenol formation and the accumulated amount of H_2O_2 is difficult to observe because of some of the side-reactions described above during the benzene oxidation, the formed H_2O_2 plays an important role in phenol formation. The V species on the calcined V/SiO_2 catalyst appeared yellow in color to the naked eye. The reaction solution including the leached V species showed a slight blue color during the initial stages and became yellow during the benzene oxidation reaction. The oxidation state of the yellow V species is well-known to be +5, and the blue V species are considered to be reduced states, probably more stable V^{4+} species. The presence of reduced V species such as V^{4+} will be due to the reduction of the V^{5+} species by ascorbic acid present in the reaction solution. From these results, the reaction scheme of phenol formation by benzene oxidation over V/SiO_2 catalysts can be postulated to proceed through a Fenton type scheme:[1,15] the first step is the formation of hydrogen peroxide by the reaction of oxygen with a proton and the reduced V (V^{4+}) species, which were produced by the reduction of the V^{5+} species by ascorbic acid. Hydroxyl radicals produced by the reaction of the formed H_2O_2 with the reduced V (V^{4+}) species and protons are considered to participate in the phenol formation. One of the plausible reaction schemes is shown in Scheme 1.



Scheme 1

The increase in the concentration of ascorbic acid caused a decrease in the phenol yield and the production of pyrocatechol, of which the yield increased with increasing ascorbic acid. Pyrocatechol is considered to be formed through a consecutive hydroxylation of the phenol formed. The increase in the amount of ascorbic acid will promote the formation of H_2O_2 and $OH^{\bullet}$ through the increase in the reduced V (V^{4+}) species [steps (2) and (3)], and the accumulated H_2O_2 and $OH^{\bullet}$ will be used to further hydroxylate the formed phenol to catechol. The increase in the acid concentration caused a decrease in the yield of phenol (Fig. 11). The hydroxycyclohexadienyl radical can react with protic acid to form benzene through dehydration [Scheme 2, steps (6) and (7)], in



Scheme 2

place of the reaction of the hydroxycyclohexadienyl radical with the V^{5+} species to produce phenol.

The yellow color based on the V^{5+} species on the surface of the V/SiO_2 catalyst was observed with the naked eye to become almost colorless on immersing the V/SiO_2 catalyst into an aqueous solution of ascorbic acid. This change in color is considered to be due to the reduction of the V^{5+} species on the V/SiO_2 catalyst to the reduced V species, probably a stable V^{4+} species, by ascorbic acid. The V species supported on SiO_2, the same as the V species leached into the reaction solution, will thus be easily reduced on contact with ascorbic acid in solution. The steps (1)–(5) mentioned above can be applied to both the heterogeneous V/SiO_2 and the soluble unsupported V catalysts.

Conclusions

The V supported oxides were found to catalyze the liquid-phase oxygenation of benzene to phenol using O_2 as an oxidant and ascorbic acid as a reductant. The V catalyst (V/SiO_2) supported on SiO_2, among various inorganic oxides investigated as a support, had a high catalytic activity for phenol formation. The co-impregnation of Cu in the V/SiO_2 catalyst had the effect that the leaching of the V species to the reaction solution was inhibited during benzene oxidation. The influence of the amount of V impregnated, the amount of ascorbic acid, and the concentration of AcOH in the solvent on the yield of phenol were investigated. The formation of H_2O_2 was observed during the benzene oxidation catalyzed by V/SiO_2 and the formed H_2O_2 was suggested to play an important role in phenol formation from benzene. The electronic absorption spectra of the homogeneous filtrate, including V species, leached from the V/SiO_2 catalyst in the aqueous acetic acid solvent containing ascorbic acid confirmed the presence of H_2O_2 formed in the filtrate. A plausible reaction scheme for the benzene oxidation to phenol catalyzed by V/SiO_2, in which scheme the steps of the reduction of V species and the formation of H_2O_2 are included, was proposed based on the data on the reaction and the spectroscopic results.

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