Phenol synthesis by liquid-phase oxidation of benzene with molecular oxygen over iron-heteropoly acid

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Abstract

The phenol synthesis by liquid-phase oxidation of benzene with molecular oxygen over iron-heteropoly acid (HPA) system was studied. When iron salts were used with $H_3PW_{12}O_{40}$, the highest activity was obtained. Spectroscopic studies showed that the state of the iron ion was changed after interaction with heteropoly acid (HPA) while the Keggin structure of HPA remained. The acidic nature of HPA activated benzene to form cationic species. Insoluble iron ion-exchanged heteropoly acid was obtained by partial ion exchange method, which also showed high activity on oxidation of benzene with molecular oxygen. The effects of reaction conditions were studied and the mechanism of deactivation was discussed. For the regeneration of catalytic activity, the addition of L-ascorbic acid as a reducing agent was suggested.

Keywords: Heteropoly acid; Oxidation of benzene; Phenol synthesis; Spectra

1. Introduction

Phenol has been produced by an indirect multistage process which produces equimolar acetone as a byproduct. Due to these disadvantages, the direct oxidation of benzene to phenol under mild conditions is desired.

We have designed several catalysts for oxidation of benzene to phenol by hydrogen peroxide, based on the reaction mechanism in Ref. [1]. Among them, $FeCl_3$ and $Fe(NO_3)_3$ supported on silica gel have shown high activities under atmospheric pressure at 313 K [2,3]. In the liquid-phase oxidation with hydrogen perox-

ide, the following three mechanistic requirements were proposed [1]:

(I) Both ferrous and ferric ions are necessary for the main reaction.

(II) The reaction must be carried out under acidic conditions, below pH = 2, in order to avoid further oxidation of phenol.

(III) The catalyst must be designed with moderate steric hindrance in order to avoid dimerization as a side reaction.

Among several oxide supports, silica gel gave the reaction field which satisfied conditions (II) and (III).

For the direct oxidation with molecular oxygen, either the ability to activate molecular oxygen or ability for further activation of benzene may be necessary in addition to the above men-

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tioned mechanistic requirements (I to III) for the oxidation with hydrogen peroxide.

The heteropoly acid (HPA) catalyst is known to activate molecular oxygen for catalytic oxidation [4]. In our previous paper [5], strong acid sites could be designed on insoluble solid surface of HPA by using a partial ion exchange method. Several types of transition metal incorporated HPA were also known as an inorganic porphyrin analogue and used in oxidation reactions [6]. These characteristics of HPA will meet above requirements for the design of catalysts.

In this paper, we have tested the direct oxidation of benzene to phenol with molecular oxygen by using HPA as a co-catalyst of $FeCl_2$.

IR and UV spectra were also measured to elucidate catalytic species.

2. Experimental

2.1. Reaction procedure

All the reactions were carried out in a 1.5×10^{-4} m^3 stainless steel autoclave reactor equipped with a side tube for periodical sampling through a syringe. Benzene which was dissolved in distilled water (8–13 mol/m^3, 1.0 $\times 10^{-4}$ m^3), catalyst (2 mmol as iron ion) and HPA (2 mmol) were put in a reactor.

The standard reaction conditions were as follows; 300 K, 1.0 MPa (pure molecular oxygen and a closed system), and 700 rpm.

Reaction products were analyzed by gas chromatography using a 2 m Apiezon grease L column [1].

2.2. Catalyst preparation

The iron ion-exchanged HPA catalysts which were not soluble in the reaction mixture were prepared by changing the ratio of iron carbonate to HPA via the following procedure.

(1) Iron carbonate was obtained by mixing a ferrous chloride solution and a sodium bicar-

bonate solution under N$_2$ atmosphere at room temperature.

(2) The aqueous solution of HPA ($H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) was titrated into the iron carbonate in distilled water. The partial iron ion-exchanged HPA ($H_{0.5}Fe_{1.25}PW_{12}O_{40}$, $H_{0.5}Fe_{1.25}PMo_{12}O_{40}$ and $H_{0.5}Fe_{1.75}SiW_{12}O_{40}$) could be obtained by adjusting the amount of titrated solution.

(3) The precipitates (iron ion-exchanged HPA) were dried in an oven at 363 K.

(4) The solid particles of iron ion-exchanged HPA were ground to powders and used as catalysts.

3. Results and discussion

3.1. Catalytic activities

Table 1 shows the results of oxidation of benzene by molecular oxygen. The yields of phenol based on benzene, $Y_{P,B}$ of various catalysts were compared at 10 h. The activity of $FeCl_2$ was low for molecular oxygen oxidation of benzene to phenol (Run No. 1).

Although iron supported silica gel had high activity in the oxidation with hydrogen peroxide [3], it had little activity with molecular oxygen (Run No. 2). In the previous study with hydro-

Table 1
The yield of phenol based on benzene, $Y_{P,B}$ of catalysts

Run No.	Catalyst	$Y_{P,B}$ (%)
1	$FeCl_2$	trace
2	$FeCl_2 / SiO_2$	trace
3	$H_3PW_{12}O_{40}$	nil
4	$H_4SiW_{12}O_{40}$	nil
5	$H_3PMo_{12}O_{40}$	nil
6	$H_3PW_{12}O_{40}$ [a] $+FeCl_2$	27.0
7	$H_{0.5}Fe_{1.25}PW_{12}O_{40}$	14.0
8	$H_{0.5}Fe_{1.25}PMo_{12}O_{40}$	4.2
9	$H_{0.5}Fe_{1.75}SiW_{12}O_{40}$	2.5

Reaction conditions; reaction time: 10 h, $FeCl_2$: 2 mmol, HPA: 2 mmol, 300 K, 1.0 MPa O$_2$, Iron ion-exchanged HPA: 2 mmol as iron ion.
[a] $H_3PW_{12}O_{40}$: 5 g.

gen peroxide [3], iron ions accompanied with a strong acid site was enough to oxidize benzene. In the case of oxidation with molecular oxygen, however, some additional functions to activate reactants should be required. In order to provide acid sites as well as oxidation sites, HPA was tested instead of silica gel support. HPA itself shows no activity (Run 3–5). When $FeCl_2$ was used together with $H_3PW_{12}O_{40}$ (denoted as HPA + iron salt), high activity could be obtained (Run No. 6). This means that the catalytic activity would appear by some interactions between $H_3PW_{12}O_{40}$ and $FeCl_2$.

Iron ion-exchanged HPA (denoted as Fe-HPA)also shows high activities (Run No. 7, 8 and 9). The catalytic activities are in the following order; $H_{0.5}Fe_{1.25}PW_{12}O_{40}$ > $H_{0.5}Fe_{1.25}PMo_{12}O_{40}$ > $H_{0.5}Fe_{1.75}SiW_{12}O_{40}$. The acid strength of Keggin-type HPA has been reported as follows [7]: $H_3PW_{12}O_{40}$ > $H_3PMo_{12}O_{40}$ > $H_4SiW_{12}O_{40}$ ≈ $H_4GeW_{12}O_{40}$ > $H_4SiMo_{12}O_{40}$ > $H_4GeMo_{12}O_{40}$.

This order of acid strength agreed fairly well with the order of catalytic activity of HPA. These suggest that the activation of benzene by strong acid sites is essential for the oxidation with molecular oxygen.

3.2. Spectroscopic studies

3.2.1. Solid tablets

Fig. 1(a) shows IR spectra of solid tablets of the $H_3PW_{12}O_{40}$ and $H_{0.5}Fe_{1.25}PW_{12}O_{40}$ catalyst, respectively. The samples show the intense 1056, 960, 888 and 815 cm^{-1} bands which are assigned to $\nu(P–O)$, $\nu(W=O)$, corner-sharing $\nu(W–O–W)$ and edge-sharing $\nu(W–O–W)$ of the Keggin structure, respectively [8]. No significant changes in the IR spectra a and b were observed before ($H_3PW_{12}O_{40}$) and after the iron ion-exchange of HPA ($H_{0.5}Fe_{1.25}PW_{12}O_{40}$). Therefore, the Keggin structure is concluded to be kept after the ion exchange. The original Keggin structure was also kept in the case of $H_{0.5}Fe_{1.25}PMo_{12}O_{40}$ and $H_{0.5}Fe_{1.75}SiW_{12}O_{40}$ after the ion exchange (not shown).

a

b
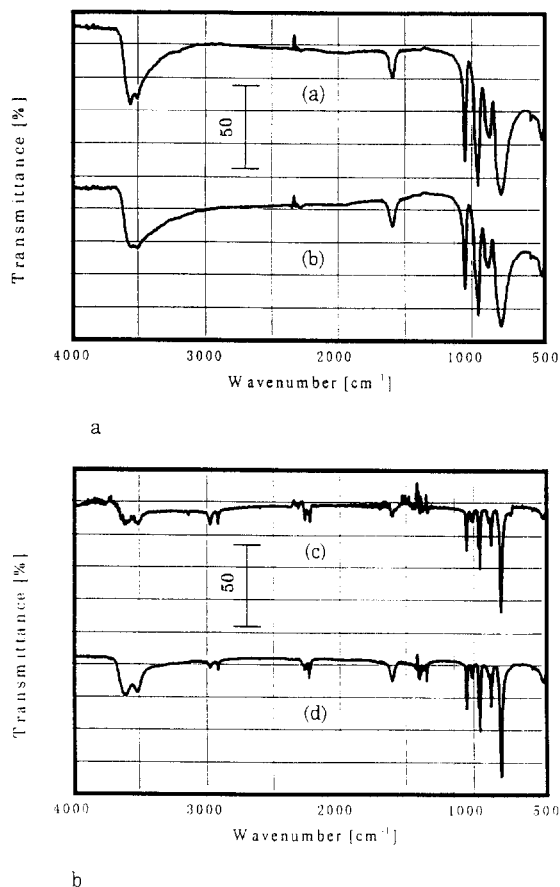
Fig. 1. (a) IR spectra of solid tablets, a: $H_3PW_{12}O_{40}$, b: $H_{0.5}Fe_{1.25}PW_{12}O_{40}$. (b) IR spectra of acetonitrile solutions, c: $H_3PW_{12}O_{40}$, d: $H_3PW_{12}O_{40}$ + $FeCl_2$.

3.2.2. Solutions

Spectroscopic studies were also conducted with soluble HPA + iron salts system as a model of insoluble ion-exchanged Fe-HPA system.

Fig. 1(b) shows IR spectra of the solution of $H_3PW_{12}O_{40}$ (spectrum c) and the mixed solution of $H_3PW_{12}O_{40}$ and $FeCl_2$ (spectrum d) in acetonitrile, respectively.

No significant changes are observed on both the solutions with and without $FeCl_2$. This suggests that the Keggin structure remains even if there are some interactions between $H_3PW_{12}O_{40}$ and $FeCl_2$ to appear the catalytic activity (Run 6 in Table 1).

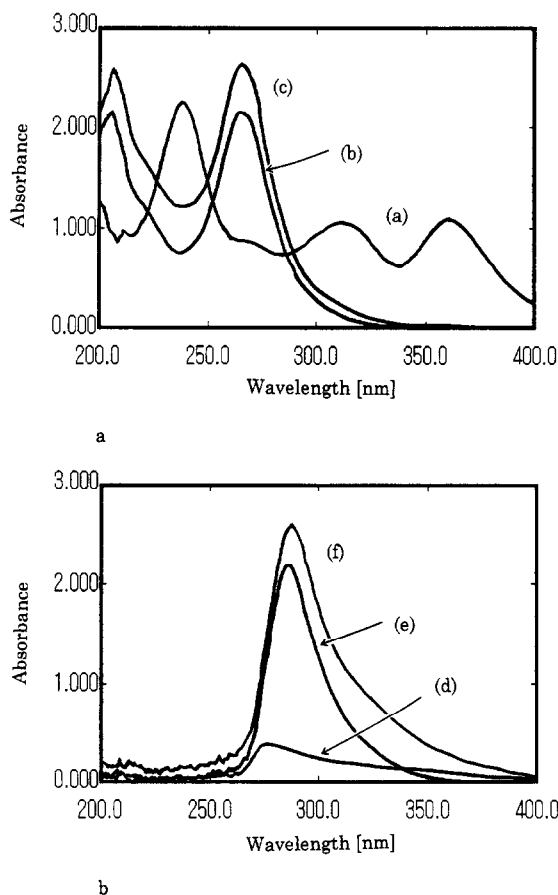Fig. 2(a) shows UV spectra of acetonitrile solutions. Spectrum a shows characteristic peaks

Fig. 2. (a) UV spectra of acetonitrile solutions, a: $FeCl_2$ (3.33 mol/m^3), b: $H_3PW_{12}O_{40}$ (0.33 mol/m^3), c: $FeCl_2$ (0.33 mol/m^3)+$H_3PW_{12}O_{40}$ (0.33 mol/m^3). (b) UV spectra of aqueous solutions with benzene, d: $FeCl_2$ (2.0 mol/m^3). e: $H_3PW_{12}O_{40}$ (0.2 mol/m^3), f: $FeCl_2$ (0.2 mol/m^3)+$H_3PW_{12}O_{40}$ (0.2 mol/m^3).

of $FeCl_2$ at 238, 312, and 360 nm while spectrum b shows peaks of $H_3PW_{12}O_{40}$ at 206 and 266 nm. The characteristic peaks of $FeCl_2$ are almost disappeared in the mixed solution of $FeCl_2$ and $H_3PW_{12}O_{40}$ (spectrum c). This suggests that the iron ion may be interacting with $H_3PW_{12}O_{40}$ and then the electronic structure will be changed while the Keggin structure of HPA remains as seen from IR studies.

Fig. 2(b) shows the results when catalysts were charged into the reaction mixture (H_2O + benzene). Spectrum d for $FeCl_2$ has a weak peak at 277 nm. Three peaks of $FeCl_2$ in acetonitrile solution (spectrum a) are masked because

of high sensitivity of benzene which has strong peaks around 250 nm as B-band (A_{1g}–B_{2u}).

The peak was shifted to 288 nm and the intensity was enhanced when $H_3PW_{12}O_{40}$ was charged to the solution (spectrum e). The shift was almost the same with $FeCl_2$ + $H_3PW_{12}O_{40}$ mixture (spectrum f).From spectroscopic studies, Timofeeva et al. [9] suggested the formation of carbonium ions and aromatic cation radicals when methylbenzenes and polycyclic arenes were charged on $H_3PW_{12}O_{40}$.

In this work, it is suggested from the shift of peak that benzene might be activated by the acidic nature of HPA to form a cationic intermediate form.

The information on the activation of oxygen had not been obtained from IR and UV spectroscopic studies.

3.3. Phenol yields

Fig. 3 compares the time course of phenol yield on $FeCl_2$ + $H_3PW_{12}O_{40}$ and $H_{0.5}Fe_{1.25}PW_{12}O_{40}$. For the mixture of $FeCl_2$ + $H_3PW_{12}O_{40}$, the reaction proceeded rapidly at the initial stage and stopped at 4 h. The final yield of phenol was about 25%. On the other hand, the initial activity of $H_{0.5}Fe_{1.25}PW_{12}O_{40}$ was lower than $FeCl_2$ + $H_3PW_{12}O_{40}$ but the
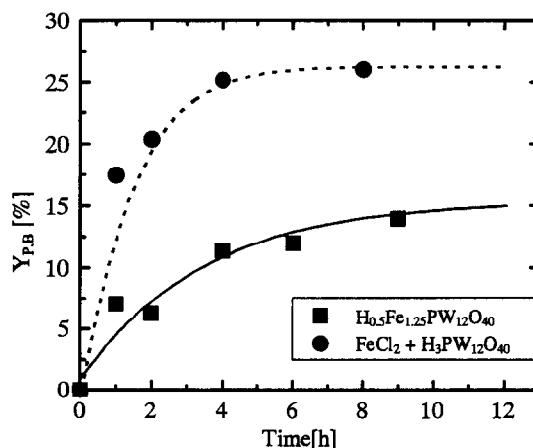
Fig. 3. Catalytic activities of $FeCl_2$ with $H_3PW_{12}O_{40}$ and $H_{0.5}Fe_{1.25}PW_{12}O_{40}$. $H_{0.5}Fe_{1.25}PW_{12}O_{40}$: 2 mmol as iron ion; $FeCl_2$: 2 mmol; $H_3PW_{12}O_{40}$: 5 g; 300 K; 1.0 MPa.

Fig. 4. Effect of oxygen pressure $H_{0.5}Fe_{1.25}PW_{12}O_{40}$: 2 mmol as iron ion; 300 K.
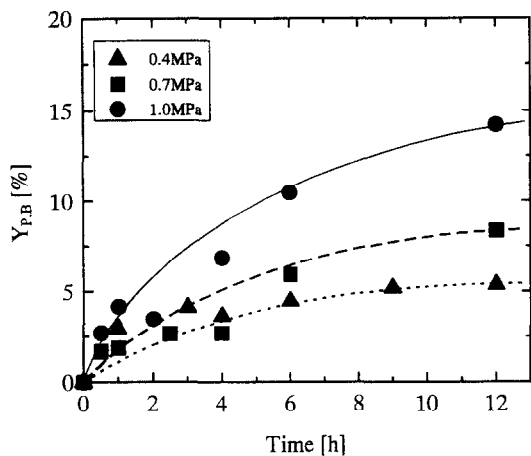

Fig. 5. Effect of reaction temperature $H_{0.5}Fe_{1.25}PW_{12}O_{40}$: 2 mmol as iron ion; 1.0 MPa.

activity was kept even after 4 h. The reaction system with $FeCl_2 + H_3PW_{12}O_{40}$ was homogeneous while that with $H_{0.5}Fe_{1.25}PW_{12}O_{40}$ was heterogeneous. In our reaction conditions, no detectable amount of biphenyl was observed on both catalysts, however, some steric hindrance has to be designed according to design requirement (III) in order to avoid side reactions (dimerization). This preferred the insoluble solid catalyst system. Also in the practical view point, insoluble catalyst is much convenient even the initial rate of reaction is lowered due to the heterogeneity.

Fig. 4 shows the effect of oxygen pressure on the phenol yield over $H_{0.5}Fe_{1.25}PW_{12}O_{40}$. The initial rate of phenol production was positively dependent on oxygen pressure. If the oxygen pressure be increased higher than 1.0 MPa, the phenol production could be accelerated.

Fig. 5 shows the effect of reaction temperature on the phenol yield over $H_{0.5}Fe_{1.25}PW_{12}O_{40}$. The initial rate was increased with the increase of temperature. The yield of phenol was increased continuously with time at 280 K and 300 K, but it stopped at 3 h at higher temperatures than 300 K.

One of the possible reasons of stop of the reaction after several hours at higher temperatures could be the irreversible oxidation of ac-
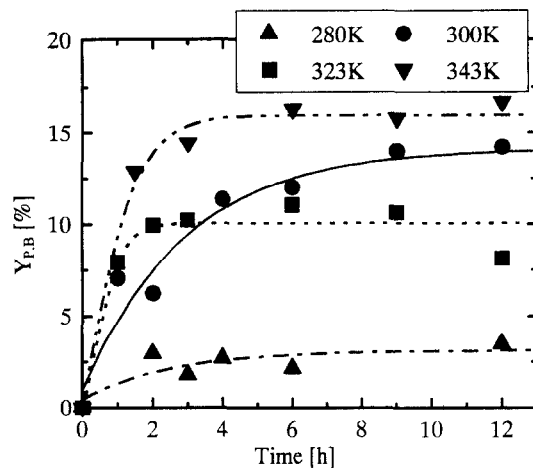
tive iron species. In order to reduce the deactivated iron ion (the accumulation of ferric ions), a suitable reducing agent is needed. According to several studies on biomimetic oxidation with iron ion [10,11], L-ascorbic acid was used as a reducing agent.

Fig. 6 shows the effect of L-ascorbic acid addition during the reaction on $H_{0.5}Fe_{1.25}PW_{12}O_{40}$ catalyst at 300 K. It was added to the reaction mixture at 12 h during the reaction. The reaction rate and phenol yield were remarkably increased after L-ascorbic acid addition.
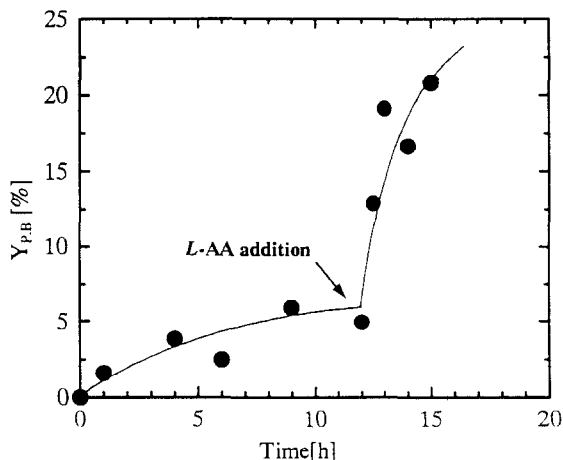

Fig. 6. Effect of reductive addition $H_{0.5}Fe_{1.25}PW_{12}O_{40}$: 0.85 mmol as iron ion: 300 K; 1.0 MPa; L-AA: 0.85 mmol.
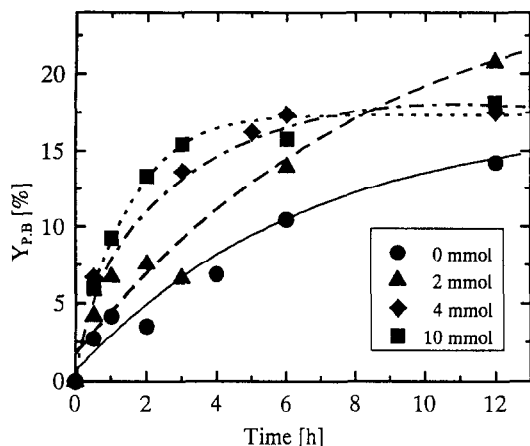
Fig. 7. Effect of L-ascorbic acid addition as a reducing agent $H_{0.5}Fe_{1.25}PW_{12}O_{40}$: 2 mmol as iron ion; 300 K; 1.0 MPa.

Fig. 7 shows the effect of the amount of L-ascorbic acid addition to the reaction mixture over $H_{0.5}Fe_{1.25}PW_{12}O_{40}$ catalyst at 300 K. The yield of phenol was promoted at the initial stage when L-ascorbic acid was added. The initial activity was increased with the increase of the amount of L-ascorbic acid added. But, the final yield was not increased so much when L-ascorbic acid was added in excess. This may be due to the catalytic oxidation of L-ascorbic acid as a side reaction. Therefore, the continuous addition of reducing agent is preferred.

4. Conclusion

Phenol synthesis by liquid-phase oxidation of benzene with molecular oxygen over iron ion-HPA catalyst was studied.

1. Both HPA + iron ion catalyst and ion exchanged Fe-HPA catalyst showed high activity to phenol synthesis.
2. IR studies showed that the Keggin structure of HPA remained in both cases and a homo-geneous HPA + Fe system could be used as a model for heterogeneous Fe-HPA catalysts.
3. UV studied showed that the electronic structure of iron species was changed for the mixed solution of HPA and $FeCl_2$.
4. The active species could activate benzene to a cationic form due to the acidic nature of HPA.
5. The deactivation was observed due to the oxidation of iron species.
6. L-ascorbic acid was effective as a reducing agent to regenerate active iron species.

Acknowledgements

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