

Liquid Phase Hydroxylation of Benzene to Phenol with Hydrogen Peroxide Catalyzed by Fe(III)/TiO₂ Catalysts at Room Temperature

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Abstract: Liquid phase hydroxylation of benzene to phenol with hydrogen peroxide on Fe(III)/TiO₂ catalysts was examined at room temperature. The catalytic performances of various TiO₂ supports were tested. The TiO₂ (JRC-TIO-1, anatase) having the highest surface area and pore volume appeared to be the most suitable support because it offered the highest activity and selectivity. The effects of the Fe(III) precursor and Fe(III) loading were investigated. The catalyst prepared from iron(III) acetylacetonate with 5 wt% Fe(III) loading was selected as a suitable catalyst. From tests of seven solvents, it was found that acetone gave the highest conversion and yield; however, acetonitrile may also be attractive because it offered high selectivity. Biphasic operation, introduced by adding more amount of solvent, did not show a potential improvement because the dilution effect seemed to play an important role in the reaction system. Finally, it was revealed that increasing the amount of ascorbic acid helped increase the conversion by enhancing the decomposition of H₂O₂ to hydroxyl radicals. However, it suppressed the formation of Fe(III), which resulted in a decrease in the degree of phenol formation. In addition, phenol can be further reacted with excess hydroxyl radicals to yield hydroquinone, benzoquinone, and catechol, resulting in a decreased selectivity.

Keywords: hydroxylation of benzene, phenol production, hydrogen peroxide, Fe(III), TiO₂

Introduction

Phenol is an important intermediate for the synthesis of various petrochemical and agrochemical products. Commercial phenol production is mainly based on the cumene process [1]. Because this process produces acetone as a co-product, which will be oversupplied in the future, and the cumene hydroperoxide intermediate can decompose violently, the development of an alternative process is desired. A number of studies have been focused on the direct oxidation of benzene to phenol.

There are two main pathways for the direct oxidation of benzene to phenol; i.e., gas phase and liquid phase reactions. Gas phase hydroxylation of benzene with ni-

trous oxide has been conducted in a pilot facility [2]. However, this process is suitable only when a supply of nitrous oxide is available, for example, as a by-product from adipic acid synthesis. Major problems arise when adapting this process to industrial applications because of catalyst deactivation by heavy coke formation and the low phenol selectivity of nitrous oxide [2]. In addition, the process is operated at an elevated temperature (higher than 573 K) and results in marginal conversion, resulting in undue high costs. Liquid phase hydroxylation of benzene to phenol is operated at room temperature or temperatures normally not higher than 353 K. H₂O₂ or O₂ is employed as an oxidant. High selectivity can be obtained with lower oxidant cost when compared with the gas phase operation. Therefore, many researchers have focused on this route and have aimed to develop suitable catalysts for the reaction.

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Table 1. Materials and Chemicals

Metal source	Iron(III) acetylacetonate, 97 % (Aldrich) Iron(III) nitrate monohydrate, 98 % (SIGMA) Iron(III) chloride hexahydrate, 99 % (MERCK)
Support	TiO ₂ (JRC-TIO1, JRC-TIO4) (Catalysis Society of Japan) TiO ₂ , 99 % (Fluka) Titanium(IV) dioxide, powder, 99.8 % (Aldrich)
Solvent	Acetone, 99.8 % (Carlo Erba) Acetonitrile, 99.8 % (MERCK) 1- Butyl alcohol, 99 % (Fluka) <i>tert</i> -Butyl alcohol, 99 % (Fluka) Dichloromethane, 99 % (Carol Erba reagenti) Ethyl alcohol, 99.9 % (Carol Erba reagenti) Pyridine, 99.7 % (MERCK)
Reducing agent	Ascorbic acid, 99.7 % (Polskie Odczynniki Chemiczne S.A.)
Substrate	Benzene, 99.7 % (MERCK)
Oxidant	Hydrogen peroxide, 30 % wt. (MERCK)
By-product reference	Biphenyl, 99.9 % (Fluka) Catechol, 98 % (Fluka) Phenol, 99 % (Panreac Sintesis) Quinol, 99.8 % (APS) 1,4 Benzoquinone, 98 % (ACROS)

Several kinds of metal, such as Fe, Cu, and V, were loaded on various supports, such as SiO₂, Al₂O₃, HZSM-5, MCM-41, and TiO₂ [3-6]. Fe-containing catalysts have drawn some attention from researchers for the hydroxylation of benzene to phenol because of its low cost and acceptable yield. Seo and coworkers [3,7] studied the use of Fe(II) and Fe(III) on SiO₂. Various Fe precursors, i.e., FeCl₃, FeCl₂, and Fe(NO₃)₃, were investigated. Fe(III) from FeCl₃ as precursor showed good performance for the hydroxylation of benzene to phenol; the addition of acidic compounds strongly affected the catalytic performance.

The solvent is usually added to the reaction system to dissolve hydrogen peroxide and benzene into one phase for the oxidation of benzene to phenol. Several solvents, such as acetone, acetonitrile, acetic acid, pyridine and dichloromethane, have been employed [8-14]. However, there are only a few studies that have compared the effects of various solvent types. Stockmann and coworkers [10] studied the oxidation of benzene to phenol using amorphous microporous mixed-oxide catalyst. Acetonitrile showed the highest yield among several solvents; i.e., 2-propanol, dimethyl glycol, and propylene glycol. On the other hand, some researchers have studied solvent-free systems from an environmental viewpoint. Low conversion and yield are usually reported.

TiO₂ has been used extensively as a catalyst and support

for oxidation and photooxidation reactions [15-19]. It is widely accepted that OH[•] radicals can also be generated on illuminated TiO₂ surfaces [20]. TiO₂ photocatalysis has been applied to the hydroxylation of benzene to phenol, but the conversion efficiency in this photocatalysis was lower than that of the Fenton process. Therefore, surface modifications of TiO₂ should be performed. The presence of electron acceptors, i.e., Fe and O₂, enhanced the photocatalytic reaction [20]. In addition, recent studies have found that Cu-, Fe-, and V-containing catalysts gave high yields of phenol [12,13]. It should be noted that comparison of the reaction performance of different systems published in the open literature is rather difficult because of differences in various parameters, such as the types and amounts of catalysts, supports, oxidants, and solvents and also differences in operating conditions such as the operating temperature and pressure.

In this study, the liquid phase hydroxylation of benzene to phenol with hydrogen peroxide on various Fe(III)/TiO₂ catalysts at room temperature was investigated. Several TiO₂ supports were tested. TiO₂ has been used as a support for many oxidation reactions. It was also reported to offer high performance for the oxidation of benzene to phenol [20]. The effects of the type of Fe(III) precursor and the Fe(III) loading were studied to find a suitable catalyst. The catalytic performances of the systems with different types of solvent and under biphasic/triphasic operations were compared. In addition, the influence of the amount of ascorbic acid as a reducing agent was considered.

Experimental

Materials and Chemicals

Table 1 summarizes the materials and chemicals employed in this work. All chemicals were used without prior purification. Four types of TiO₂ supports, i.e., TiO₂ (JRC-TIO-1), TiO₂ (JRC-TIO-4), TiO₂ (Fluka), and TiO₂ (Aldrich), and three types of Fe(III) precursors, i.e., iron(III) acetylacetonate, iron(III) chloride hexahydrate, and iron(III) nitrate monohydrate, were used in the study.

Catalyst Preparation

Fe(III)/TiO₂ catalysts were prepared by impregnation of TiO₂ support powder in a solution of Fe(III) precursor at 353 K, followed by evaporation and drying overnight. The catalysts obtained were calcined in a furnace continuously fed with air (flow: 60 cm³/min). The temperature was increased from room temperature to 773 K at a heating rate of 10 K/min and then held for 5 h to remove organic residues. After calcination, the catalysts were stored in a desiccator.

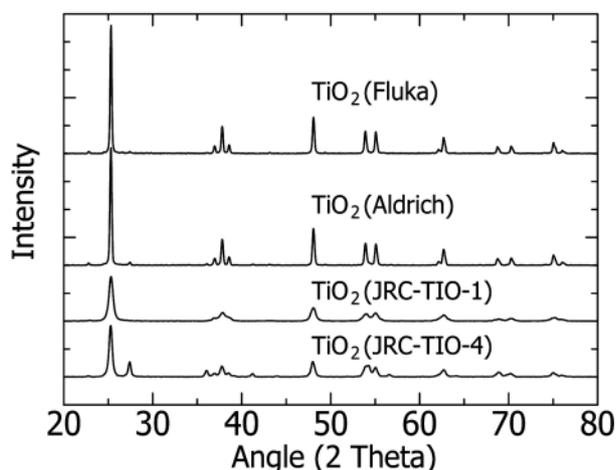
Table 2. Catalytic Performance of Commercial TiO₂ Supports

Catalyst	Conversion ^a (%)	Selectivity ^b (%)	BET surface area (m ² /g)	Pore volume (cm ³ /g)
TiO ₂ (JRC-TIO1, anatase)	0.8	100	76.6	0.29
TiO ₂ (JRC-TIO4, anatase)	0.2	72	51.8	0.11
TiO ₂ (Fluka, anatase)	0.4	100	16.5	0.03
TiO ₂ (Aldrich, anatase)	0.1	70	8.0	0.02
TiO ₂ (JRC-TIO1, rutile)	0.03	100	1.8	0.003
TiO ₂ (Fluka, rutile)	0.01	100	1.7	0.002

(Benzene = 11 cm³; catalyst weight = 0.2 g; benzene/H₂O₂ mole ratio = 0.5; temperature = 303 K; pressure = 1 atm; reaction time = 4 h)

^a Conversion calculated as moles of benzene reacted per initial moles of benzene*100 %

^b Selectivity calculated as moles of phenol per mole of benzene reacted*100 %

**Figure 1.** XRD patterns of TiO₂ supports.

Characterization

XRD patterns of the TiO₂ supports and Fe(III)/TiO₂ catalysts were obtained by using a SIEMENS D 5000 X-ray diffractometer, with Cu K α radiation and equipped with a Ni filter; range of detection (2θ): 20~80; resolution 0.04.

The BET surface areas and porosities of the catalysts were measured by a Micromeritics ASAP 2020 instrument. A sample of 0.3 g was degassed at 573 K for 3 h and the amount of N₂ adsorbed was observed.

XPS surface analysis was performed using Kratos Amicus X-ray photoelectron spectroscopy. The XPS spectra were measured using the following conditions: Mg K α X-ray source at current of 20 mA and 12 keV, resolution of 0.1 eV/step, and pass energy of 75 eV. The operating pressure was ca. 1×10^{-6} Pa. A wide-scan survey spectrum was collected for each sample to determine the elements present on the surface. All the binding energies were calibrated internally with the carbon C 1s photoemission peak at 285.0 eV. Photoemission peak areas were determined after smoothing and background subtraction using a linear routine. Deconvolution of complex spectra was done by fitting with Gaussian (70 %)-Lorentzian (30 %) shapes using the VISION 2 software that came with the XPS system.

Experimental Setup and Product Analysis

The hydroxylation of benzene by H₂O₂ was carried out in a 125-cm³ round-flat-bottomed flask at 303 K and 1 atm with high-speed stirring at 600 rpm. In a typical experiment, 0.5 g of ascorbic acid (2.8 mmol) was added in a liquid mixture containing 40 cm³ of solvent, 30 cm³ of H₂O₂ (0.32 mol), and 11 cm³ of benzene (0.16 mol). It should be noted that the typical experiment was operated in a triphasic system consisting of solid catalyst, solvent phase, and aqueous phase. When more solvent was added to the system, the reaction might have occurred in the biphasic system comprising the solid catalyst and solvent phase.

The feed and products were analyzed by a gas chromatograph (SHIMADZU 9A) equipped with a packed column of GP 10 % SP-2100. The operating conditions of the GC were as follows: injection temperature of 523 K, detector temperature of 523 K, initial column temperature of 383 K, final column temperature of 443 K, and temperature programmed rate of 10 K/min. The products were also analyzed by GC-MS, especially for some product species that could not be detected by the FID detector. The benzene conversion is defined as the number of moles of benzene consumed by the reaction divided by the initial number of moles of benzene, while the phenol selectivity is defined as the number of moles of generated phenol divided by the number of moles of benzene consumed.

Results and Discussion

Selection of TiO₂ Supports

TiO₂ was used as a catalyst support for the hydroxylation of benzene to phenol. TiO₂ supports were characterized by XRD. The similar XRD patterns shown in Figure 1 indicate that all of the supports were of the anatase phase [21]. The blank reaction tests of the TiO₂ supports were performed under solvent-free conditions. The results shown in Table 2 reveal that TiO₂ (JRC-TIO-1) offered the highest conversion, which corresponded with it also having the highest BET surface area and pore

Table 3. Effects of %Fe(III) Loading and Type of Fe(III) Precursor on Catalytic Performance

Precursor	Fe loading (%)	Conversion ^a	Selectivity ^b	Yield ^c	TOF ^d	TON ^e	BET ^f	Pore volume ^g
Fe(III) aca	1	4.7	25	1.19	13.83	55.34	74.4	0.26
	5	10.8	21	2.29	5.32	21.30	68.5	0.25
	10	13.2	20	2.65	3.08	12.32	64.3	0.22
	20	14.8	18	2.63	1.53	6.11	57.9	0.19
Fe(III) Cl	1	4.2	29	1.23	14.26	57.03	72.4	0.27
	5	9.2	23	2.16	5.02	20.09	69.1	0.24
	10	11.2	20	2.21	2.57	10.28	64.8	0.23
	20	12.8	18	2.24	1.30	5.21	58.5	0.2
Fe(III) N	1	5.1	24	1.23	14.29	57.15	70.1	0.26
	5	11.2	19	2.13	4.95	19.81	65.4	0.23
	10	13.7	16	2.16	2.51	10.04	59.9	0.22
	20	16.1	14	2.20	1.28	5.12	54.2	0.18

(Benzene = 11 cm³; catalyst weight = 0.2 g; benzene/H₂O₂ mole ratio = 0.5; acetone solvent = 40 cm³; ascorbic acid = 0.5 g; temperature = 303 K; pressure = 1 atm; reaction time = 4 h)

^a Conversion calculated as moles of benzene reacted per initial moles of benzene*100 %

^b Selectivity calculated as moles of phenol per mole of benzene reacted*100 %

^c Yield calculated as moles of phenol per initial moles of benzene*100 %

^d Turnover frequency calculated as moles of phenol per mole of Fe per h

^e Turnover number calculated as moles of phenol per mole of Fe

^f BET surface area (m²/g)

^g Pore size volume (cm³/g)

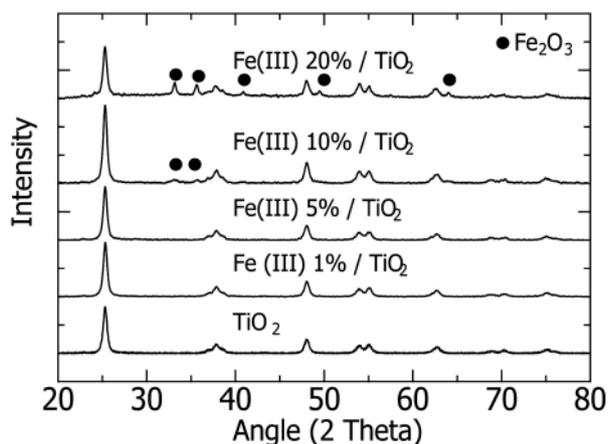


Figure 2. XRD patterns of Fe(III)/TiO₂ at various % loading (Fe(III) acetylacetonate as precursor).

volume. TiO₂ (JRC- TIO-1) and TiO₂ (Fluka) were further converted to the rutile phase by calcination at 773 K for 20 h. The reaction tests reveal that although TiO₂ in the rutile phase still maintained high selectivity (100 %), the conversion became much lower, which corresponded with the significant reduction of its BET surface area and pore volume. It should be noted that the obtained conversion was significantly low and, therefore, loading with metal catalyst was needed. Thus, TiO₂ (JRC-TIO-1) in the anatase phase was selected as a support for all of the following experiments.

Effects of Fe(III) Precursor and Fe(III) Loading

Fe(III)/TiO₂ catalysts were prepared from three precursors: Fe(III) acetylacetonate, Fe(III) chloride hexahydrate, and Fe(III) nitrate monohydrate, abbreviated as Fe(III) acac, Fe(III) Cl, and Fe(III) N, respectively. Because the TiO₂ surface is hydrophilic, the precursors in hydrate form or having water as a solvent should allow the uniform distribution of Fe metal in the catalysts. The XRD patterns of samples with various percentages of Fe(III) loadings (in the case of Fe(III) acac as precursor) are shown in Figure 2. The obvious peaks of Fe(III) in Fe₂O₃ crystallize were observed only at a Fe(III) loading of 20 %. The relationship between the Fe(III) loading at surface determined by XPS and the Fe(III) loading is shown in Figure 3. The results indicate that the metal was located more at the surface of TiO₂ than in the pores. In addition, it is clear that the type of precursor influenced the metal distribution in the catalysts. The accessibility of Fe(III) into the catalyst pores followed the order Fe(III) Cl > Fe(III) acac ≈ Fe(III) N.

The effects of the Fe(III) loading on the benzene conversion, phenol selectivity, and yield for different catalysts are summarized in Table 3. The values of the turnover frequency, turnover number, BET surface area, and pore volume are also provided. The byproducts from the reaction system were hydroquinone, benzoquinone, and catechol. The experimental results indicated that the conversion increased with increasing Fe(III) loading, while the selectivity decreased, thus an optimum yield was ob-

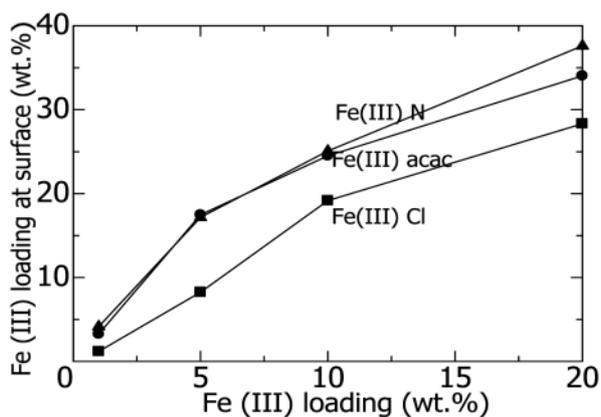


Figure 3. Relationship between %Fe on surface and %Fe(III) loading for different Fe precursors.

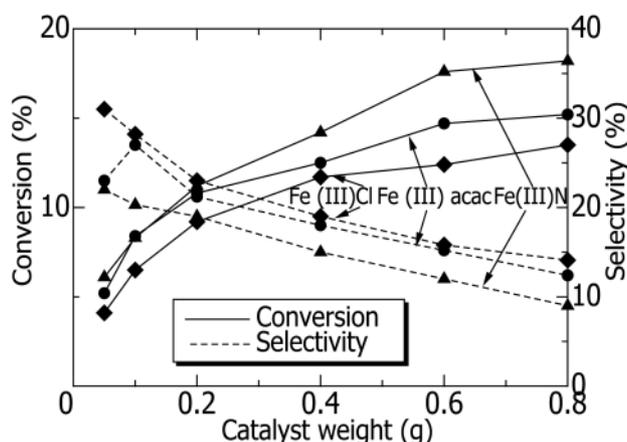


Figure 4. Effect of catalyst weight on benzene conversion and phenol selectivity for different Fe(III) precursors.

served. The increases in conversion were obtained as a result of the increased amount of metal active species. However, when considering the values of TOF and TON, it is noticed that the metal active sites were utilized less efficiently at high Fe(III) loadings. This situation is likely to be due to the reduced BET surface area and pore volume. The increase in yield was less pronounced when the Fe(III) loading was higher than 5 wt%. Therefore, this value was selected as an optimum Fe(III) loading for all precursors.

Figure 4 shows the catalytic performances of Fe(III)/TiO₂ catalysts prepared from the three precursors at different catalyst weights. The Fe(III) loading of the catalysts was 5 wt%. The benzene conversion increased, but the phenol selectivity decreased, upon increasing the amount of catalyst. This situation because phenol can be further reacted to give catechol, benzoquinone, and hydroquinone, which are undesirable by products. The catalytic activity followed the order Fe(III) N > Fe(III) acac > Fe(III) Cl; however, the selectivity followed the opposite order. From the corresponding yields (Figure 5), the

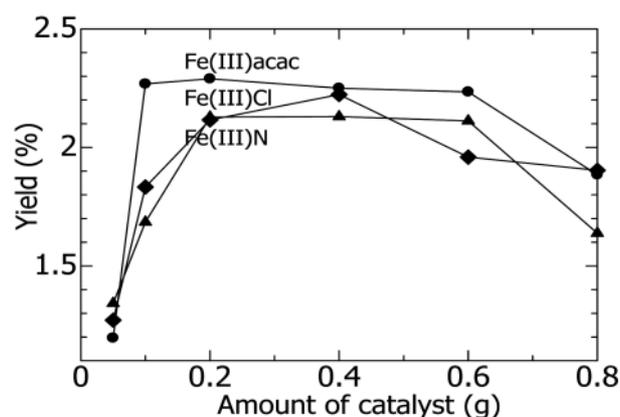


Figure 5. Effect of catalyst weight on phenol yield for different Fe(III) precursors.

most suitable precursor and catalyst weight were Fe(III) acac and 0.2 g, respectively.

It should be noted that the type of Fe(III) precursor influenced the metal distribution of the catalyst and its catalytic performance. It is likely that the reaction took place mainly at the catalyst surface because the rank of the catalytic activity observed from the benzene conversion in Table 3 followed the same trend as that shown in Figure 3 for all values of catalyst loading. In addition, the type of catalyst precursor may not significantly govern the selectivity. As shown in Figure 4, for example, when the conversion was ca. 12.5 %, the corresponding values of selectivity of Fe(III) N, Fe(III) acac, and Fe(III) Cl were ca. 15.5, 17, and 15 %, respectively, i.e., they were essentially equivalent. However, further studies are required to consider this situation in more detail.

Effect of Type of Solvent and Biphasic/Triphasic Operation

Solvent was used to reduce the mass transfer resistance by helping dissolve H₂O₂ into the benzene phase. Under the standard conditions with a solvent volume of 40 cm³, the reaction was performed in a triphasic system comprising the solid catalyst, organic phase, and aqueous phase. The oxidation performances of the system with different solvents are summarized in Table 4. High yields were obtained for acetone, dichloromethane, and acetonitrile, respectively. Acetone offered the highest benzene conversion and phenol yield, but low selectivity. Acetonitrile might be a good alternative solvent because it provided very high selectivity with a yield as high as that obtained when using dichloromethane as solvent. From these observations, acetone and acetonitrile were further considered to compare the catalytic performance in biphasic and triphasic operations.

Figure 6 shows the catalytic performance of the reaction system using different amounts of solvent; i.e., 40, 60, and 80 cm³. In the case of acetone, the system changed

Table 4. Effect of Solvent Type on the Catalytic Performance of Fe(III)/TiO₂ Catalysts

Solvent	Conversion ^a (%)	Selectivity ^b (%)	Yield ^c (%)	TOF ^d (1/h)	TON ^e (-)
Acetone	10.8	21.2	2.3	5.32	21.3
Dichloromethane	2.2	62	1.4	3.18	12.7
Acetonitrile	1.3	97	1.3	2.93	11.7
Pyridine	0.8	92	0.7	1.73	6.9
<i>tert</i> -Butyl alcohol	1.5	47	0.7	1.65	6.6
1-Butyl alcohol	1.5	10	0.2	0.35	1.4
Ethyl alcohol	1.3	8	0.1	0.25	1

(Benzene = 11 cm³; % Fe(III) loading = 5 wt%; catalyst weight = 0.2 g; benzene/H₂O₂ mole ratio = 0.5; solvent = 40 cm³; ascorbic acid = 0.5 g; temperature = 303 K; pressure = 1 atm; reaction time = 4 h)

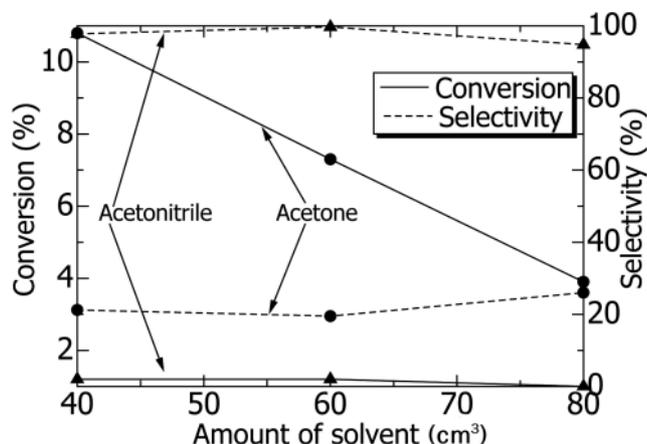
^a Conversion calculated as moles of benzene reacted per initial moles of benzene*100 %

^b Selectivity calculated as moles of phenol per mole of benzene reacted*100 %

^c Yield calculated as moles of phenol per initial mole of benzene*100 %

^d Turnover frequency calculated as moles of phenol per mole of Fe per h

^e Turnover number calculated as moles of phenol per mole of Fe

**Figure 6.** Effect of amount of solvent on benzene conversion and phenol selectivity.

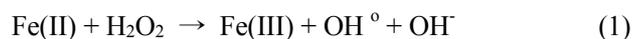
from triphasic to biphasic at 60 cm³. The benzene conversion dramatically decreased, while the selectivity increased slightly, when the system changed to biphasic and when more solvent was added in the biphasic system. In the case of acetonitrile, the system remained triphasic at 60 cm³ and became biphasic at 80 cm³. An almost insignificant effect of the amount of acetonitrile on the conversion and selectivity was observed, at least within the range of this study. Although it was expected that operation in biphasic systems would eliminate the presence of interfacial mass transfer resistance and, consequently, improve the catalytic performance of the reaction system, the dilution effect, as well as the poor mixing induced by the addition of extra solvent, retarded any such improvement. For both solvent cases, biphasic operation did not have a beneficial effect on the catalytic performance. This situation was particularly obvious in the case of acetone as solvent, which offered much lower performance. It should be noted that for the case of ace-

tonitrile, which is not an inert solvent but participates directly in the reaction [10], no significant drop in the catalytic performance was observed upon increasing the amount of solvent. This study suggests that selection of a suitable amount of solvent is important, but operation in a biphasic system is not always advantageous.

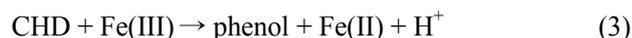
Effect of the Amount of Ascorbic Acid

The amount of ascorbic acid was varied between 0.5 and 5 g using two types of solvent; i.e., acetone and acetonitrile.

The mechanism of Fenton's method is widely accepted as follows:



The hydroxyl radical reacts directly with benzene to produce cyclohexadienyl (CHD) radical, which subsequently undergoes an H⁺ abstraction as follows [22,23]:



However, the CHD radical intermediate can react with H⁺ and collapse to benzene as follows:



Ascorbic acid is well known as a good reducing agent. It changes the state of the metal catalyst from Fe(III) to Fe(II).

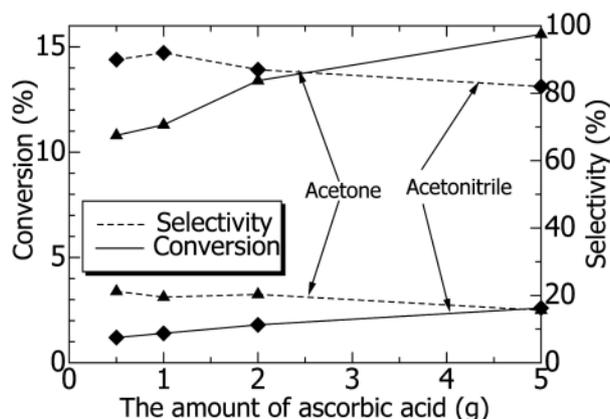
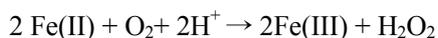
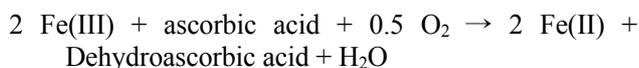


Figure 7. Effect of amount of ascorbic acid on benzene conversion and phenol selectivity.



Both Fe(III) and Fe(II) play important roles in the reaction system. Fe(III) helps to catalyze the conversion of the CHD radical intermediate to phenol, while Fe(II) promotes the decomposition of hydrogen peroxide to hydroxyl free radicals. The amount of generated hydroxyl radicals which affects phenol formation, could be controlled by the amounts of ascorbic acid and metal catalyst added.

As shown in Figure 7 the benzene conversion increased with increasing the amount of ascorbic acid, while the selectivity decreased slightly, in both the acetone and acetonitrile systems.

This situation can be explained by considering that increasing the amount of ascorbic acid activated the state change from Fe(III) to Fe(II), which enhanced the decomposition of H_2O_2 to hydroxyl radicals (as shown in Eq. 1) and, consequently, increased the benzene conversion (Eq. 2). However, too much ascorbic acid, which functioned as a reducing agent, suppressed the formation of Fe(III), which resulted in a decrease in the formation of phenol via the H^+ abstraction of CHD (Eq. 3). In addition, CHD can easily collapse to benzene when the Fe(II) content increased (Eq. 4) and also phenol can be further reacted with excess hydroxyl radicals to yield catechol, hydroquinone, and benzoquinone, resulting in the decrease of selectivity.

It should be noted that ascorbic acid was highly soluble in the aqueous phase, but not in the organic phase. The addition of solvent was necessary to promote the reaction in this system by dissolving H_2O_2 , ascorbic acid, and benzene into one phase.

Conclusion

The liquid phase hydroxylation of benzene to phenol with hydrogen peroxide catalyzed by Fe(III)/TiO₂ catalysts was investigated. The most suitable Fe(III) precursor and %Fe(III) loading were iron(III) acetylacetonate and 5 wt%, respectively. Among the solvents studied (acetone, dichloromethane, acetonitrile, pyridine, *tert*-butyl alcohol, 1-butyl alcohol, and ethyl alcohol), acetone showed the highest conversion and yield, but low selectivity. However, acetonitrile may be an attractive solvent because of its high selectivity. Biphasic operation was not attractive compared to triphasic operation because of the dilution effect. Benzene conversion increased with increasing the amount of ascorbic acid; however, too much ascorbic acid retarded the yield improvement because of lower phenol selectivity.

Acknowledgment

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