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Phenol oxidation into catechol and hydroquinone over H-MFI, H-MOR, H-USY and H-BEA in the presence of ketone

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Abstract

Phenol oxidation with hydrogen peroxide into catechol (CL) and hydroquinone (HQ) over H-MFI, H-MOR, H-USY and H-BEA in the presence of diethylketone was investigated. Among the examined zeolites, large pore zeolites having 12-membered oxygen ring aperture, H-MOR, H-USY and H-BEA, showed higher reaction yield than that having 10-membered oxygen ring aperture, H-MFI. The reaction yield over these zeolites was in the order of H-BEA > H-USY > H-MOR > H-MFI, thus the superior one was H-BEA in this work. The sum of the reaction yield of CL and HQ based on hydrogen peroxide was >89% over H-BEA ($SiO_2/Al_2O_3 = 150$) in the presence of diethylketone at 373 K for 5 min reaction.
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1. Introduction

Phenol oxidation into catechol (CL) and hydroquinone (HQ) is an industrially very important process because CL and HQ are widely used as starting materials for medicine, perfume and many fine chemicals. Typical industrial phenol oxidation process has been conducted with acid catalyst. For example, in patent literatures [1,2], inorganic acid such as sulfuric acid and zeolites were used as catalyst. Also very important progresses were reported in patent literatures that the addition of organic molecules such as ketone into both the sulfuric acid [3] and zeolites [4] catalytic system improved reaction yield. However, the role of the added ketone in the oxidation has not been clear.

The reaction yields and selectivity based on hydrogen peroxide with sulfuric acid and zeolites are comparable in most cases [1–4]. However, if the complicatedness of separation of acid component from oxidation products mixture and neutralizing treatment of this are concerned, solid acid such as zeolite is more preferable [5]. Therefore, we focused our interest on zeolite catalytic system. At first, we examined catalytic activity of H-MFI (H-ZSM-5), H-mordenite

(H-MOR), H-ultrastable Y (H-USY) and H-beta (H-BEA) themselves for the oxidation of phenol with hydrogen peroxide. Then, we investigated the effect of the addition of diethylketone on the reaction yield of phenol oxidation over these zeolites.

In addition, the activity of zeolites was compared with that of sulfuric acid, which is an example of industrial catalyst, in the presence and absence of diethylketone, respectively. Molecular size was estimated by periodic molecular mechanics calculation. In this calculation, a size of the cell occupied by a molecule in a periodic condition was used as a measure of void space by the molecule. The void space was used for intuitive discussion concerning to diffusion resistance of molecules in zeolite pore. From these results, we discussed the role of diethylketone in the phenol oxidation.

2. Experimental

Powder form H-MFI (UOP/Nikki universal, $SiO_2/Al_2O_3 = 40$, proton form), H-MOR (UOP/Nikki universal, $SiO_2/Al_2O_3 = 18$, proton form), H-USY (UOP/Nikki universal, $SiO_2/Al_2O_3 = 18$, proton form) and H-BEA (zeolyst, $SiO_2/Al_2O_3 = 25$ and 150, ammonium and proton form, respectively) were used after calcination at 823 K in air for more than 2 h. Reagent grade phenol, diethylketone

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and 96% sulfuric acid (Wako) were used without further purification. Sixty percent aqueous solution of hydrogen peroxide used in this work was industrial products of Kemira-UBE Industries.

The oxidation reactions were done in a round-bottomed flask equipped with a water-cooled condenser and a magnetic stirrer. Under an atmosphere of dry nitrogen the mixture of 10.00 g of phenol and 0.20 g of zeolite in the flask were heated up to a reaction temperature using an oil bath. An amount of 0.27 g of diethylketone was added into the reaction mixture if the effect of diethylketone was investigated. While, 0.02 g of sulfuric acid was added in place of zeolite when the catalytic activity of sulfuric acid was examined. All reactions reported in this work were conducted at 373 K of the oil bath temperature. At the reaction temperature 0.10 g of 60% hydrogen peroxide aqueous solution was added into the reaction mixture at 0, 1.5, 3.0 min, so that the total amount of added hydrogen peroxide was 0.3 g. The reaction temperature was maintained for 5 min, and then cooled to room temperature. The products were analysed by means of Hitachi 263-70 gas chromatograph equipped with both a 2 m glass column of 3% OV-17 supported gaschrom Q (80/100 mesh) and an FID detector. Biphenyl was used as internal standard for the gas chromatograph analysis.

3. Calculation

The molecular size was calculated for diethylketone, phenol, hydrogen peroxide, catechol and hydroquinone by periodic molecular mechanics optimization. Cerius2_4.6/OFF and compass force field set (Accelrys) were used for the calculation. Calculations were done as follows. (1) A molecule was put in a rectangular periodic cell. (2) Structure of the molecule and cell volume were optimized while cell angles
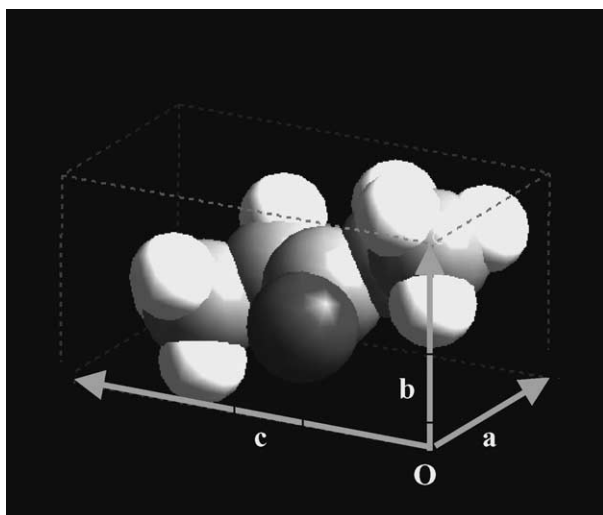
were fixed at α, β and $\gamma = 90°$. The cell size was optimized in which a molecule feeling force exerted by replicas in surrounding cells. Therefore, the optimized cell size is expected to be roughly equal to void space by a molecule. Diethylketone in an optimized periodic cell is shown in Fig. 1 as a typical result. The cell lengths (a, b and c) were listed in Table 4 and used as a measure of size of a molecule.

4. Results and discussion

4.1. Phenol oxidation over zeolite

Prior to investigate the effect of the addition of diethylketone, we examined catalytic activities of H-MFI, H-MOR, H-USY and H-BEA zeolites in the absence of diethylketone. The pore aperture sizes of these zeolites are listed in Table 1. Results of the phenol oxidation over these zeolites are shown in Table 2.

Among the zeolites examined, the reaction yield over H-MOR was the lowest, 0.61%. The colour of H-MOR after a reaction was almost black. On the other hand, the solution turned to pale yellow after a reaction. These observations suggested that coking over H-MOR occurred in a short period from the initiation of a reaction [6]. This would be due to its high acid strength of H-MOR [8,9]. Niwa and co-workers [10] reported that relative acidic strength of zeolites is in the order of H-MOR > H-MFI > H-BEA > H-Y (in our work we utilized H-USY). The strong acid site over H-MOR is expected to induce coking. The coke would block the pore and catalytic active sites of H-MOR. Therefore, it is suggested that the coking over H-MOR would inhibit both the oxidation of phenol and products.

While, as judged from the colour of catalyst after a reaction, the coking over H-MFI, H-USY and H-BEA also oc-

Fig. 1. Diethylketone placed in an optimized periodic cell. Cerius2_4.6/ OFF and compass force field (Accelrys) were used for calculation.

Table 1
Pore aperture size of zeolites

Zeolite[a]	Aperture size (nm × nm)
H-MFI (10)	0.54 × 0.56
H-MOR (12)	0.65 × 0.70
H-USY (12)	0.74
H-BEA (12)	0.64 × 0.76

[a] Number of oxygen in aperture ring are shown in parenthesis.

Table 2
Phenol oxidation over zeolite

Zeolite[a]	Yield (%)[b]			CL/HQ[c]
	CL	HQ	CL + HQ	
H-MFI (40)	10.46	4.22	14.68	2.48
H-MOR (18)	0.00	0.61	0.61	–
H-USY (18)	10.00	5.94	15.94	1.58
H-BEA (150)	27.95	3.25	31.19	8.16

[a] SiO$_2$/Al$_2$O$_3$ ratios are shown in parenthesis.
[b] Reaction yields based on added hydrogen peroxide.
[c] mol/mol ratio.

curred. However, the production of CL and HQ was fairly observed. Therefore, the coking over these zeolites was not so crucial, and the higher yields over these zeolites would be due to a moderate acid strength of these zeolites.

The reaction yields were in the order of H-BEA > H-USY ≥ H-MFI. These results indicated that a large pore zeolites having both 12-membered oxygen ring (H-BEA and H-USY) and acid sites of moderate strength act as effective catalyst. The total reaction yield, the sum of yields of CL and HQ, was highest over H-BEA. While, concerning to the yield of HQ, H-USY and H-MFI were effective than H-BEA. These results suggest that the controlling factor of CL production is different from that of HQ production over these zeolite catalysts. Therefore, if the reaction dynamics of the phenol oxidation and also side reactions over zeolite is concerned as a chemical engineering problem, the reaction schemes of CL and HQ should be assumed to be different each other.

Accumulation of tarry compounds in solution was observed over these zeolites. This indicated that, besides the coking over zeolites, a portion of the products and hydrogen peroxide was consumed by successive oxidation affording tar. Therefore, it is expected that effective retardation of successive oxidation improves the reaction yield.

In Section 4.2, we have discussed the effect of the addition of diethylketone on the reaction yield of the phenol oxidation over these zeolites.

4.2. Phenol oxidation over zeolite in the presence of diethylketone

The results of the phenol oxidation over zeolite in the presence of diethylketone are shown in Table 3. It is clear from the comparison between Tables 2 and 3 that the addition of small amount of diethylketone, 0.5 mol of hydrogen peroxide, drastically improved the reaction yield of both CL and HQ. This small amount of diethylketone was sufficient for the improvement, and the addition of more diethylketone only slightly affected the reaction yield. Some other ketone having different structure was also effective and the results will be reported in our patent literature [11].

Table 3
Phenol oxidation over zeolite in the presence of diethylketone

Zeolite[a]	Yield[b] (%)			CL/HQ[c]
	CL	HQ	CL + HQ	
H-MFI (40)	16.76	6.67	23.44	2.51
H-MOR (18)	21.80	20.84	42.64	1.05
H-USY (18)	29.53	26.39	55.92	1.12
H-BEA (150)	49.32	39.85	89.18	1.24
H-BEA (25)	45.25	36.75	82.00	1.23

[a] SiO_2/Al_2O_3 ratios are shown in parenthesis.
[b] Reaction yield based on added hydrogen peroxide.
[c] mol/mol ratio.

Table 4
Molecular size[a]

Molecule	a (nm)	b (nm)	c (nm)
Diethylketone	0.4085	0.4631	0.7939
Phenol	0.4792	0.4908	0.5090
Hydrogen peroxide	0.2476	0.2476	0.3661
Catechol	0.4857	0.4869	0.5126
Hydroquinone	0.4559	0.4934	0.5193

[a] Represented by optimized cell size obtained by periodic molecular mechanics calculation using Cerius2_4.6/OFF and compass force field set (Accelrys).

The effect of diethylketone was prominent over large pore zeolites, H-USY and H-BEA. The reaction yield of CL+HQ reached 89.18% over H-BEA having SiO_2/Al_2O_3 ratio of 150. In order to compare the catalytic reactivity of H-USY and H-BEA in a close range of SiO_2/Al_2O_3 ratio, the oxidation of phenol over H-BEA having SiO_2/Al_2O_3 ratio of 25 was conducted. The reaction yield of 82% was obtained over H-BEA having SiO_2/Al_2O_3 ratio of 25. These results indicated that the reaction yield is influenced by SiO_2/Al_2O_3 ratio. However, the reaction yield was sufficiently higher than the yield over H-USY. Therefore, it is fairly said that the combination of H-BEA and diethylketone is very probable way to construct superior, thus greener, oxidation catalytic system.

Although Ti containing analogue of H-MFI (Ti-MFI, so-called TS-1) has been known as a superior oxidation catalyst [6,7,12], the combination of H-MFI and diethylketone was not so effective. This would be due to resistance of diffusion of molecules in H-MFI pore, because the pore diameter of H-MFI is very close to the size of reactants and products (compare Tables 1 and 4).

The molecular size of diethylketone, phenol, hydrogen peroxide, catechol and hydroquinone calculated by periodic molecular mechanics using compass force field (Accelrys) are listed in Table 4. From a comparison of Tables 1 and 4, it is recognized that phenol, hydrogen peroxide, catechol and hydroquinone would diffuse easily in pore of H-MOR, H-USY and H-BEA. However, the length of diethylketone estimated from c-value of periodic cell (0.7939 nm) is larger than the aperture size of all of the zeolites. Therefore, motion of diethylketone would be more restricted than the other molecules at zeolite pore aperture. Diethylketone would be regulated to diffuse along c-axis of optimized cell (Fig. 1) through the zeolite pore aperture and, especially in H-MFI, the rotation about a- and b-axes would be strongly inhibited. From these, the resistance of diffusion in zeolite pore would be a reason of the low reaction yield over smaller pore zeolite, H-MFI.

As judged from the colour of catalyst and reaction mixture after a reaction, the extent of coking and accumulation of tarry compound are seemed to be lesser over H-BEA than H-USY. These observations suggest that the added diethylketone most effectively retard the coking and accumulation of tarry compounds over H-BEA. Thus, it is recog-

nized that the effect of diethylketone depends not only on the pore aperture size but the structure inside pore or local atmosphere at around a catalytic reaction sphere.

Although we assumed that the phenol oxidation occurs in the pore of zeolites, it should not be excluded the probability of that the oxidation might proceed outside the zeolite pore. Over H-BEA, both the yields of CL and HQ were improved by the addition of diethylketone. The extent of improvement was CL < HQ. If CL and HQ were mainly produced outside and inside the pore of H-BEA, respectively, as were the cases of TS-1 (Ti-MFI) and Ti-BEA [12], then it was suggested that diethylketone exerts its effect on both outside and inside of the pore.

In [12], the dependence of the reaction yield on crystalline size of zeolite was also discussed. They prepared two kinds of TS-1 having different crystalline sizes; those were about 0.1×10^{-6} and $45 \times 10 \times 3 \times 10^{-6}$ m. The reaction yield strongly depended on crystalline size and obtained 86.6% over 0.1×10^{-6} m crystalline and 71.5% over $45 \times 10 \times 3 \times 10^{-6}$ m crystalline at 333 K for 6 h reaction. The diffusion would control the oxidation of phenol over zeolite in the presence of ketone in this work. However, we could not investigate the dependence of the reaction yield on the crystalline size of each zeolite, because of the difficulty in controlling zeolite crystalline size. We are now planning to control SiO_2/Al_2O_3 ratio of H-BEA in the range of 25–300 and to investigate the effect of the ratio on the reaction yield, because SiO_2/Al_2O_3 ratio indeed influenced the reaction yield as described above (also see Table 3). Crystalline structure of H-BEA of each SiO_2/Al_2O_3 ratio will be observed, for example, by scanning electron microscopy, and discussed in our following paper.

The amount of added diethylketone was about 2.5 wt.% of total reaction mixture. This small amount of diethylketone would not drastically alter the bulk properties, such as dielectric constant, of a reaction mixture. Therefore, it is less probable that the added diethylketone acts as a co-solvent. However, more investigation is needed in order to make clear that whether the added diethylketone acts as a solvent or not. The added diethylketone was almost recovered after a reaction. The typical loss of diethylketone after a reaction was about ∼2%, which was estimated by GC analysis. From the detailed analysis of products mixture, it was indicated that the small amount of diethylketone was consumed by side reactions such as oxidation of diethylketone itself, for example, by the Baeyer–Villiger reaction [13].

The exact role of diethylketone in the improvement of the reaction yield in our catalyst system could not be described in detail in this work. However, ketone molecule is expected to act as follows. It is known that ketone interacts with hydrogen peroxide affording ketone peroxide species, for example R–C(OH)(OOH)–R′ [12,14]. Organic hydroperoxide has moderate reactivity than hydrogen peroxide. By virtue of this moderate reactivity, the further oxidation of products

Table 5
Phenol oxidation with sulfuric acid in the presence and absence of diethylketone

	Yield[a] (%)			CL/HQ[b]
	CL	HQ	CL + HQ	
With diethylketone	37.82	31.73	69.55	1.19
Without diethylketone	39.62	24.20	63.82	1.64

[a] Reaction yield based on added hydrogen peroxide.
[b] mol/mol ratio.

would be retarded effectively. It is also reported that ketone having fluorocarbon side chains such as CF_3COCF_3 itself catalyse the epoxidation of alkene [15]. From these, it is expected that diethylketone would act as co-catalyst in the phenol oxidation over zeolite. It is also probable that the acid property of zeolites is controlled by interaction of acid site and diethylketone. If this is main cause of the effect, then spectroscopic study of adsorbed species on zeolites will aid in understanding the cause.

In Section 4.3, in order to confirm the advantage of the combined system of zeolites and diethylketone, we investigated the phenol oxidation with sulfuric acid in the presence and absence of diethylketone, and compared with that over zeolites.

4.3. Effect of diethylketone in sulfuric acid catalysed phenol oxidation

Results of the phenol oxidation with sulfuric acid catalysed phenol oxidation [1,3] in the presence and absence of diethylketone is shown in Table 5. In the absence of diethylketone, the reaction yield of CL + HQ with sulfuric acid was higher than that obtained over any zeolites given in Table 2. The reaction yield was slightly improved by the addition of diethylketone. The improvement of the yield of HQ was larger than that of CL. This tendency is the same with that was observed over zeolites.

As a comparison, phosphoric acid (H_3PO_4) was used in the place of sulfuric acid. The oxidation of phenol did not proceed both in the presence and absence of diethylketone. Therefore, it seems likely that the acidity as strong as sulfuric acid is needed to catalyse the oxidation of phenol.

Both in the absence and presence of diethylketone, the accumulation of tarry compounds was observed. From these observations, it was indicated that inhibition of successive oxidation by the addition of diethylketone was less effective with sulfuric acid catalyst than with zeolites. The successive oxidation and, thus, accumulation of tarry compound would be induced by contact of CL or HQ with or without hydrogen peroxide over acid. Therefore, the superiority of zeolite in the phenol oxidation is probably due to spatial separation of each acid site by virtue of zeolite pore structure. Thus, it would be said that the combination of diethylketone and zeolite constitutes more effective catalytic system than with sulfuric acid.

5. Conclusion

We investigated about the phenol oxidation over zeolites, and the effect of the added diethylketone. The reaction yield of CL and HQ was in the order of H-BEA > H-USY > H-MOR > H-MFI in the presence of diethylketone. The added diethylketone was more effective for large pore zeolites, H-BEA, H-USY and H-MOR than for small pore zeolite, H-MFI. H-BEA was the superior in this work. The yield of HQ was more influenced than that of CL by the addition of diethylketone. In order to elucidate the role of diethylketone in the phenol oxidation over zeolites, we are now investigating in detail in experimental and theoretical ways. We are now controlling the acid property of zeolites, and thus the catalytic activity for the phenol oxidation [16].

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