

Iron(II)-8-quinolinol/MCM-41-Catalyzed Phenol Hydroxylation and Reaction Mechanism

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Iron(II)-8-quinolinol/MCM-41 is prepared. Its catalysis is studied in phenol hydroxylation using H₂O₂ (30%) as oxidant. The experiment shows that Iron(II)-8-quinolinol/MCM-41 has good catalytic activity and desired stability. Based on cyclic voltammetry, ESR, and UV-visible spectra studies of iron(II)-8-quinolinol complex in liquid phase, a radical substitution mechanism is proposed and used to demonstrate the experimental facts clearly. © 1997 Academic Press

INTRODUCTION

Diphenol production through phenol hydroxylation has been studied extensively since the 1970s. Cu²⁺, Au³⁺, Co²⁺ (1), Fe³⁺ (2, 3), and Fe²⁺ (4–6) have been investigated with respect to their catalysis in the hydroxylation of phenol. Although these simple metal ions have some activity in catalyzing this reaction, the reaction rate and selectivity to diphenols are not desirable. Therefore, scientists turn to studying the catalysis of metal complexes. Some complexes, such as metal-phthalocyanine (M-Pc) (7) [M = Sb, Bi, V, Mo, Sn, Sn-Mo, and Sn-Sb (7); M = Cu²⁺, Co²⁺, Mn²⁺, Fe²⁺ (8)], Fe(III)-bipyridine (9), Co(II, III)-Schiff base (10), and Co(II)bis-[3(salicylideneconine) propyl]methylamine, as well as the porphyrin complexes of group IA–VIA, IVB–VII, and VIII metal cations (11), have been investigated as catalysts in phenol hydroxylation. Although they have better catalytic activity and selectivity than the simple metal ions, these metal complex catalysts are not desirable for industrial application. This is due to the shortcomings of homogeneous catalysis, such as difficult recovery of catalysts and difficult continuous operation.

To find desirable catalysts for phenol hydroxylation, many heterogeneous catalysts have been prepared. FePc-zeolite X or Y (12), iron(III)- and manganese(III) tetramethylporphyrin-zeolite Y (13), zeolite Y-encapsulated Mn-salen [salen = *N,N*-ethylenebis(salicylideneaminato)] (14), TS-1 (15, 16), and TS-2 (17, 18) have been used to catalyze a variety of synthetically impor-

tant oxidations including phenol hydroxylation under mild conditions; however, the results have been disappointing because of the limited pore size of these catalysts, which makes it difficult for substrates to diffuse into and products to diffuse out of the narrow channel of the microporous inorganic solids (19).

Up to now, some mesoporous solids including silica (20), kanemite (21), modified layered materials (22), and MCM-41 (23) have been produced and are characterized by pore diameters that could be adjusted to between 1.8 and 20.0 nm. MCM-41 mesoporous molecular sieve possesses not only regular arrays of uniform channels, but also high surface area and exceptionally high sorption capacity of cyclohexane and benzene (23). MCM-41 thus could be used as a support for metal complexes to solve the drawback existing with the microporous zeolite-supported metal complexes.

EXPERIMENTAL

Catalyst Preparation

Until now, there have been no reports of MCM-41 as a support for iron(II)-8-quinolinol. A sample of MCM-41 (Si/Al = 20) was synthesized following several patents (23). For the as-synthesized product, interplanar spacings $d_{100} = 4.46$ nm and $d_{110} = 2.74$ nm were observed. The corresponding powder X-ray diffraction patterns of the bulk sample are shown in Fig. 1a. The BET surface area of the prepared sample is $972.4 \text{ m}^2 \text{ g}^{-1}$.

Iron(II)-8-quinolinol/MCM-41 was prepared according to the following steps. First, 5.0 g MCM-41 was mixed with 200 ml of a 0.05 mol/liter [Fe(8-quinolinol)₃]Cl₂ solution of alcohol. The mixture was then stirred for 24 h at ambient temperature, filtered, and washed with alcohol until no [Fe(8-quinolinol)₃]Cl₂ was detected in the filtrate. During this process, the complexes on the surface of MCM-41 particles and those poorly immobilized in the pore are removed. Only those complex molecules immobilized well would remain in the channels of this support.

The BET area of the fresh iron(II)-8-quinolinol/MCM-41 is $886.5 \text{ m}^2/\text{g}^{-1}$. Its X-ray diffractogram, in

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Fig. 1b, shows that MCM-41 undergoes no structural change during preparation of the catalyst. According to the infrared spectra of $[\text{Fe}(\text{8-quinolinol})_3]\text{Cl}_2$ (Fig. 2a), iron(II)-8-quinolinol/MCM-41 (Fig. 2b), and MCM-41 (Fig. 2c), MCM-41 has no IR signals in the region $1300\text{--}1600\text{ cm}^{-1}$, but iron(II)-8-quinolinol/MCM-41 and $[\text{Fe}(\text{8-quinolinol})_3]\text{Cl}_2$ have the similar infrared spectra in this region. This shows that the metal complex was immobilized in MCM-41 successfully. According to chemical analysis, the supported catalyst contains 7% mass of iron(II)-8-quinolinol. The good immobilization of iron(II)-8-quinolinol could be attributed to the adsorption and static coulombic functions between $[\text{Fe}(\text{Qx})_3]^{2+}$ species and the pore wall of MCM-41.

Reaction Conditions and Analytical Methods

Phenol hydroxylation was carried out in a 25-ml glass reactor equipped with a thermostatic jacket, reflux condenser, submerged cooler, thermometer, and magnetic stirrer. Catalyst, phenol, and solvent were added successively into the reactor. The reaction was initiated by adding H_2O_2 (30 mass%) at the set temperature. Products were analyzed on a gas chromatograph using a flexible glass capillary column coated with XE-60. Programmed temperature was adopted for product analysis, with the initial temperature 100°C and the final temperature 190°C .

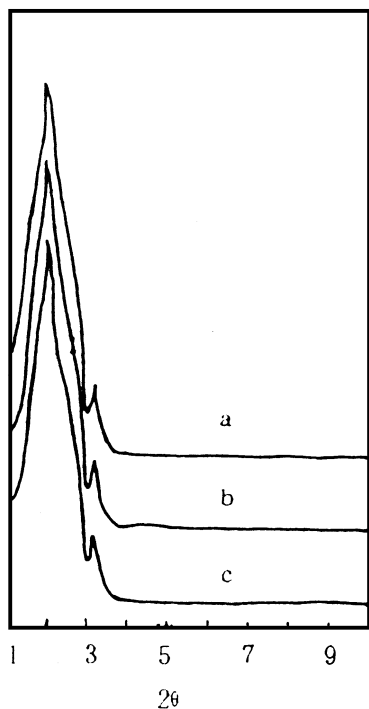


FIG. 1. XRD patterns of MCM-41 (a), fresh iron(II)-8-quinolinol/MCM-41 (b), and the used iron(II)-8-quinolinol/MCM-41 (c) after 10 runs.

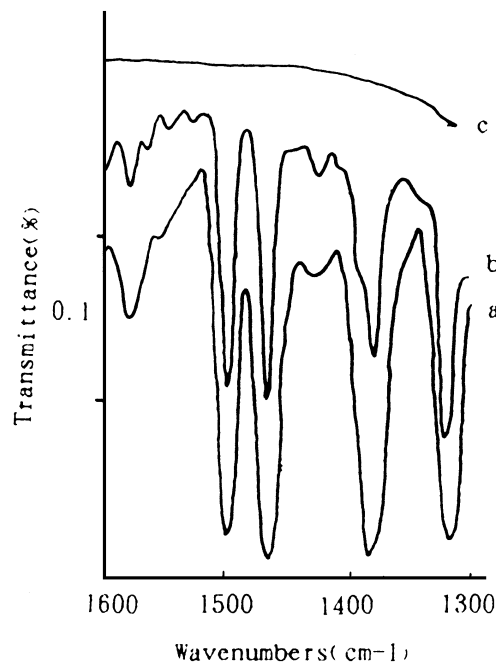


FIG. 2. Infrared spectra of $[\text{Fe}(\text{Qx})_3]\text{Cl}_2$ (a), fresh iron(II)-8-quinolinol/MCM-41 (b), and MCM-41 (c).

Infrared spectra were recorded on a Bio-Rad FTS-7(USA) IR spectrophotometer; X-ray diffraction powder patterns were recorded with a Rigaku D/max-qB X-ray diffractometer (Japan). The UV-visible (UV-Vis) studies were carried out with a Specord UV-Vis (Zeiss, Jena). The ESR study was carried out with a JES-FE3AX ESR spectrometer (Japan). Cyclic voltammetry was carried out on a Model 500 AC Impedance Analyzer (CH Instrument Co.), which was equipped with a cell stand, a Ag/AgCl reference electrode, and a platinum wire counter electrode. The working electrode used was a glassy carbon disk electrode.

RESULTS AND DISCUSSIONS

Catalytic Activity

The catalytic activities of iron(II) ion, iron(II)-8-quinolinol, iron(II)-8-quinolinol/MCM-41, MCM-41, and TS-1 in phenol hydroxylation were studied. The results, in Table 1, show that phenol and H_2O_2 cannot react without the participation of catalysts under the experimental conditions. It was also observed that Fe^{2+} (Fenton reagent) and iron(II)-8-quinolinol had poor average turnover frequency. Moreover, more by-products of benzoquinone and oxygen were also not good for diphenol production when Fe^{2+} (Fenton reagent) was used as catalyst. When iron(II)-8-quinolinol was immobilized in MCM-41, the average turnover frequency of iron(II)-8-quinolinol/MCM-41 was about two times that of iron(II)-8-quinolinol. On

TABLE 1

Catalytic Activity Comparison of Iron(II)-8-quinolinol/MCM-41, Iron(II)-8-quinolinol, MCM-41, and Other Catalysts in the Phenol Hydroxylation^a

Catalyst	Phenol conversion (%)	Product selectivity (%)			O ₂ evolved (ml)	TOF ^b (h ⁻¹)
		CAT	HQ	PBQ		
No catalyst	0.0	—	—	—	0	0
8-Quinolinol	0.0	—	—	—	0	0
MCM-41	0.0	—	—	—	0	0
Fe ²⁺ (Fenton reagent)	20.5	68.7	18.9	12.4	35	17.6 ^c
Fe(II)-Qx	25.8	65.3	32.7	2.0	25	18.1 ^c
TS-1 ^d	27.0	53.0	47.0	0.0	20	13.8 ^e
Fe(II)-Qx/MCM-41	48.2	57.5	41.8	0.7	8	33.9 ^c

CAT, catechol; HQ, hydroquinone; PBQ, *p*-benzoquinone; Fe(II)-Qx, iron(II)-8-quinolinol.

^a Reaction time: 6 h; temperature: 50°C; reaction medium: water; pH 7.0; concentration of phenol: 0.35 mol/liter; molar ratio phenol/H₂O₂: 1.0; volume of reacting mixture: 15 ml. Catalyst used: MCM-41 molecular sieve, 100 mg; Fe(II)-Qx/MCM-41, 100 mg (containing 7 mg [Fe(Qx)₃]Cl₂); [Fe(Qx)₃]Cl₂, 7 mg; Fe²⁺, same moles as for 7 mg [Fe(Qx)₃]Cl₂; 8-quinolinol, 7 mg.

^b Average turnover frequency.

^c The active site is Fe²⁺ or [Fe(Qx)₃]Cl₂.

^d For TS-1 [Ti/(Ti + Si) = 0.021]; phenol/catalyst (g/g) = 10; other conditions are the same as those for the above-mentioned catalysts.

^e The active site is Ti⁴⁺ in TS-1.

one hand, this increase may be due to the concentration of substrates in the channels of MCM-41; on the other hand, it might be attributed to the distortion of iron(II)-8-quinolinol by the pore wall of MCM-41. The distortion might activate substrates and/or catalyst, which would make the phenol hydroxylation proceed well. Table 1 also shows that iron(II)-8-quinolinol/MCM-41 has a higher average turnover frequency than the commercial catalyst TS-1.

Iron(II)-8-quinolinol/MCM-41 was used in 10 runs to catalyze phenol hydroxylation with little decrease in catalytic activity; phenol conversion in the 10th run was about 85% that in the first run. The X-ray diffractogram of the catalyst used for the 10 runs is shown in Fig. 1c, and is similar to those of fresh iron(II)-8-quinolinol/MCM-41 (Fig. 1b) and MCM-41 (Fig. 1a). According to chemical analyses, loss of the immobilized metal complex during the 10 runs of reaction was 9.5%. The preceding indicates that the support MCM-41 did not change its structure during phenol hydroxylation and iron(II)-8-quinolinol had good immobilization in MCM-41.

When phenol hydroxylation catalyzed by iron(II)-8-quinolinol/MCM-41 was carried out in different solvents, such as water, acetonitrile, acetone, and cyclohexane, different results were obtained (shown in Table 2).

Meanwhile, it was observed that the pH of the reaction system also had great effects on the phenol hy-

TABLE 2

Effects of Reaction Medium on the Phenol Hydroxylation Catalyzed by Iron(II)-8-quinolinol/MCM-41^a

Reaction medium	Phenol conversion (%)	Product selectivity (%)			O ₂ evolved (ml)	TOF ^b (h ⁻¹)
		CAT	HQ	PBQ		
Water	48.2	57.5	41.8	0.7	8	33.9 ^c
Acetonitrile	26.4	56.8	30.7	12.5	5	18.6 ^c
Acetone	3.5	56.3	20.1	23.6	1	2.5 ^c
Cyclohexane	0.0	—	—	—	0	0 ^c

CAT, catechol; HQ, hydroquinone; PBQ, *p*-benzoquinone.

^a Reaction time: 6 h; temperature: 50°C; reaction medium: water; pH 7.0; concentration of phenol: 0.35 mol/liter; molar ratio of phenol/H₂O₂: 1.0; volume of reaction mixture: 15 ml; iron(II)-8-quinolinol/MCM-41: 100 mg.

^b Average turnover frequency.

^c The active site is [Fe(Qx)₃]Cl₂.

droxylation catalyzed by iron(II)-8-quinolinol/MCM-41 (Table 3).

Mechanism of the Phenol Hydroxylation Catalyzed by Free and Supported Iron(II)-8-quinolinol

The typical voltammogram of iron(II)-8-quinolinol is shown in Fig. 3, which indicates that E_{pc} and E_{pa} are 1.0 and 0.93 V, respectively. Based on their difference ΔE (70 mV), this redox reaction could be considered reversible. According to the equation $E^0 = 1/2(E_{pa} + E_{pc})$, the potential of the redox couple iron(II/III)-8-quinolinol is 0.965 (V). The potential of the redox couple H₂O₂/H₂O is 1.77 V (24). The large potential difference of these two redox couples can easily lead to a redox reaction between H₂O₂ and iron(II)-8-quinolinol.

Generally, H₂O₂ is considered to have a skew chain structure. The bond energies between two atoms in hydrogen peroxide are helpful in predicting the production of active

TABLE 3

Effects of pH on the Phenol Hydroxylation Catalyzed by Iron(II)-8-quinolinol/MCM-41^a

pH	Phenol conversion (%)	Product selectivity (%)			O ₂ evolved (ml)	TOF ^b (h ⁻¹)
		CAT	HQ	PBQ		
1	20	58.2	40.9	0.9	5	14.1 ^c
2	57.5	56.0	36.8	7.2	10	40.4 ^c
4	53.2	56.3	38.6	5.1	9	37.2 ^c
7	48.2	57.5	41.8	0.7	8	33.9 ^c
9	8.5	57.9	42.5	0.0	15	6.0 ^c
12	0.0	0.0	0.0	0.0	20	0 ^c

For abbreviations, see Table 2.

^a The reaction conditions are the same as those in Table 2.

^b Average turnover frequency.

^c The active site is [Fe(Qx)₃]Cl₂.

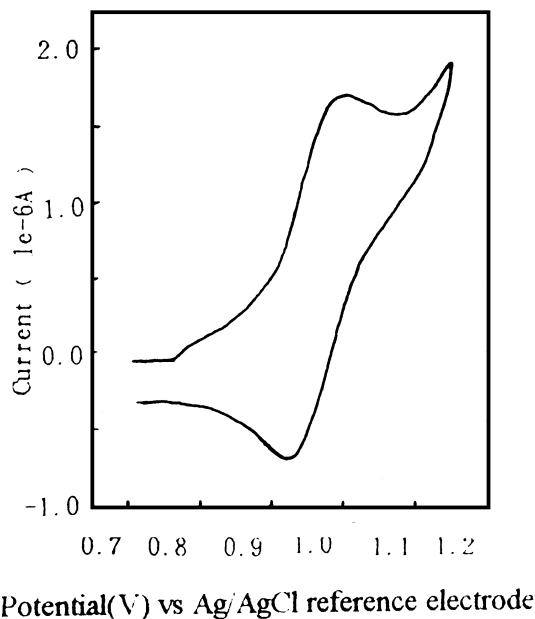


FIG. 3. Cyclic voltammogram of iron(II)-8-quinolinol in 0.1 M KCl solution. Scan rate: 1 mV/s.

species in oxidation. The bond energies of O-H and O-O in H_2O_2 can be obtained from the energies of a number of reactions (25).

Table 4 shows that the O-O bond is more easily broken than the O-H bond in the H_2O_2 molecule. The p orbital along the O-O bond direction in the H_2O_2 molecule would thus get one electron from another substance to produce $\cdot OH$. In the phenol hydroxylation catalyzed by free and supported iron(II)-8-quinolinol, on one hand, H_2O_2 may receive one electron from iron(II)-8-quinolinol to produce iron(III)-8-quinolinol and active species $\cdot OH$; on the other hand, iron(III)-8-quinolinol could also be reduced to iron(II)-8-quinolinol. This can be confirmed by ESR and UV-Vis spectra studies of iron(II)-8-quinolinol.

The UV-Vis spectra of iron(II/III)-8-quinolinol complexes are shown in Fig. 4 and are in accordance with those reported in the literature (26). The spectral changes induced by addition of H_2O_2 the solution of iron(II)-8-quinolinol are shown in Fig. 5. In Figs. 4 and 5, the transformation of iron(II)-8-quinolinol into iron(III)-8-quinolinol is

TABLE 4

Energies of a Number of Reactions Related to the Breaking of the Bonds of H_2O_2

Reaction	Reaction	Energy needed to break bonds (kcal/mol)
1	$H_2O_2 \rightarrow 2 \cdot H + 2 \cdot O$	254.9
2	$H_2O_2 \rightarrow 2 \cdot OH$	52.6
3	$H_2O_2 \rightarrow 2 \cdot H + O_2$	136.6
4	$H_2O_2 \rightarrow \cdot H + HO_2^{\cdot}$	90

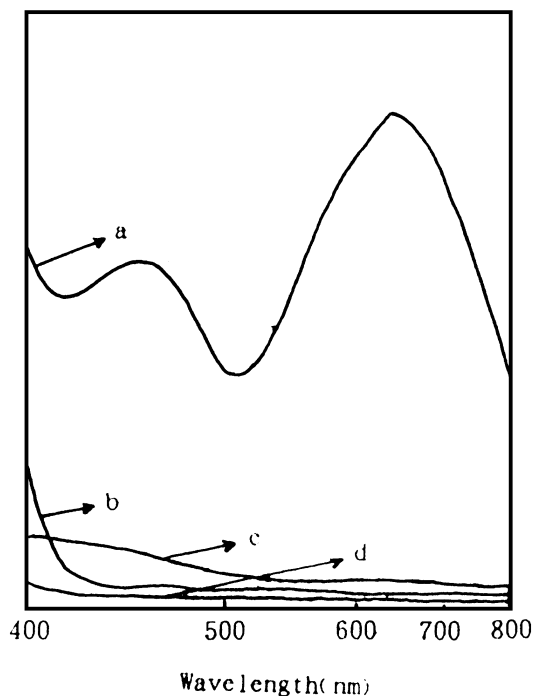


FIG. 4. UV-visible spectra of iron(III)-8-quinolinol (a), 8-quinolinol (b), iron(II)-8-quinolinol (c), and H_2O_2 (d) in the visible region.

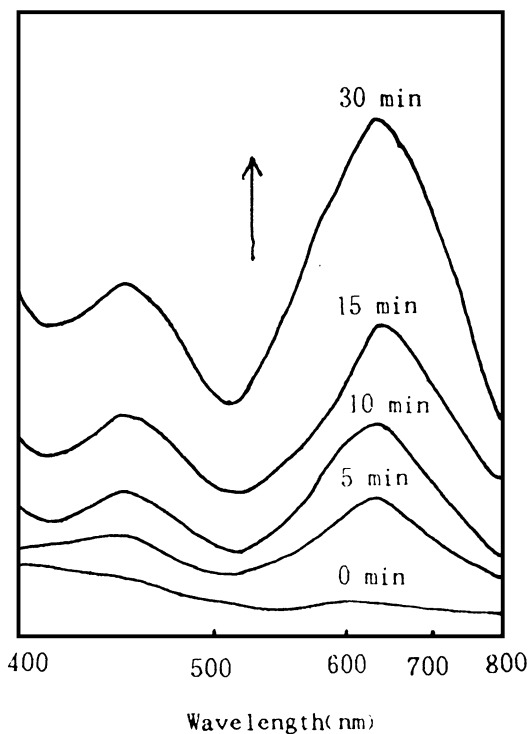


FIG. 5. UV-visible spectral change of iron(II)-8-quinolinol (2×10^{-4} mol/liter) + H_2O_2 (2×10^{-4} mol/liter) + H_2O system ($50^\circ C$) (time was recorded at the beginning of addition of H_2O_2).

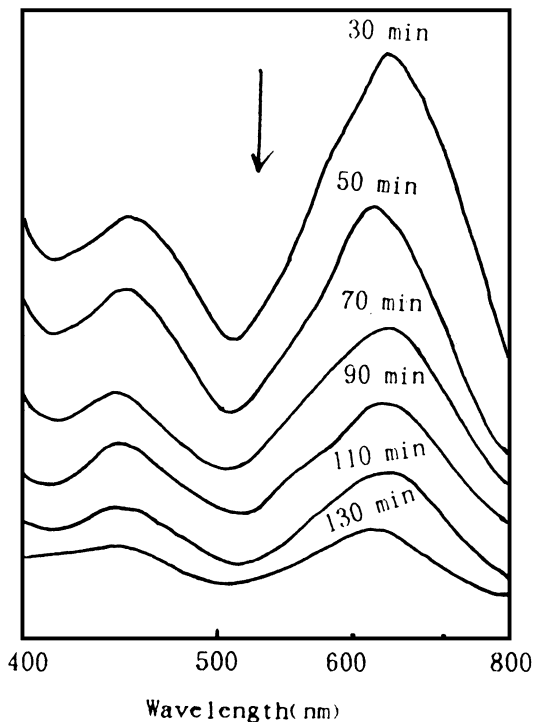


FIG. 6. UV-visible spectral change of the system described in Fig. 5, when phenol (4×10^{-4} mol/liter) is added to this system at 30 min.

demonstrated clearly. In Fig. 6, when phenol was added to the iron(II)-8-quinolinol + H_2O_2 + H_2O system at 30 min, it was observed that iron(III)-8-quinolinol was slowly reduced to iron(II)-8-quinolinol again. According to gas chromatographic analysis, catechol and hydroquinone were produced in this process.

The transformation of iron(II)-8-quinolinol into iron(III)-8-quinolinol in the iron(II)-8-quinolinol + H_2O_2 + H_2O system was also confirmed by ESR. Water solutions of iron(II)-8-quinolinol, iron(III)-8-quinolinol, and the iron(II)-8-quinolinol + H_2O_2 + H_2O system were individually transferred into capillary tubes and then used for ESR studies. The ESR spectra of iron(II)-8-quinolinol and iron(III)-8-quinolinol, in Fig. 7, show that iron(II)-8-quinolinol has no ESR signals, but iron(III)-8-quinolinol does. When H_2O_2 was added to the iron(II)-8-quinolinol solution, the ESR spectrum of iron(III)-8-quinolinol appeared (Fig. 8), and its peak height also increased with time. This means that part of the iron(II)-8-quinolinol was oxidized to iron(III)-8-quinolinol. When phenol was added 30 min after H_2O_2 was, the spectral change shown in Fig. 9 occurred, confirming the transformation of iron(III)-8-quinolinol into iron(II)-8-quinolinol.

Table 1 shows that MCM-41 and ligand 8-quinolinol have no catalytic activity for phenol hydroxylation, but iron(II)-8-quinolinol and supported iron(II)-8-quinolinol/MCM-41 do. This means that iron(II)-8-quinolinol is the key substance in catalyzing this reaction in both homogeneous and

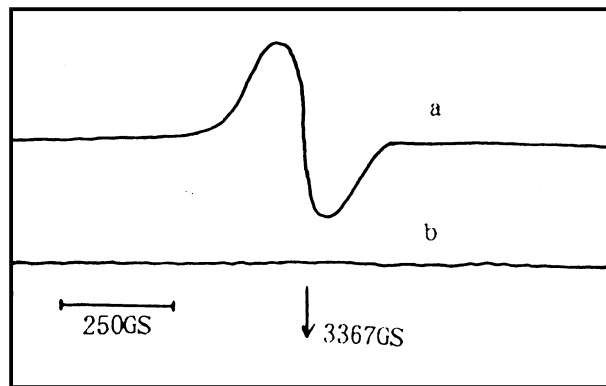


FIG. 7. ESR spectra of $[\text{Fe}(\text{Qx})_3]^{3+}$ (10^{-4} mol/liter) (a) and $[\text{Fe}(\text{Qx})_3]^{2+}$ (10^{-4} mol/liter) (b).

liquid-solid phases. Therefore, iron(II)-8-quinolinol and iron(II)-8-quinolinol/MCM-41 should have the same catalytic reaction mechanism in phenol hydroxylation.

Based on the above studies of catalytic activity and ESR and UV-Vis spectra, a reaction mechanism was proposed for phenol hydroxylation catalyzed by free and supported iron(II)-8-quinolinol (Scheme 1).

This mechanism shows that steps 1 and 3 are very important for phenol hydroxylation, which has been confirmed by UV-Vis (Figs. 5, 6) and ESR (Figs. 8, 9) spectral studies. For step 2, $\cdot\text{OH}$ is an electrophile, which differs from the nucleophile OH^- , so it tends to have an electrophilic attack at the *ortho* and *para* positions of the phenol molecules to

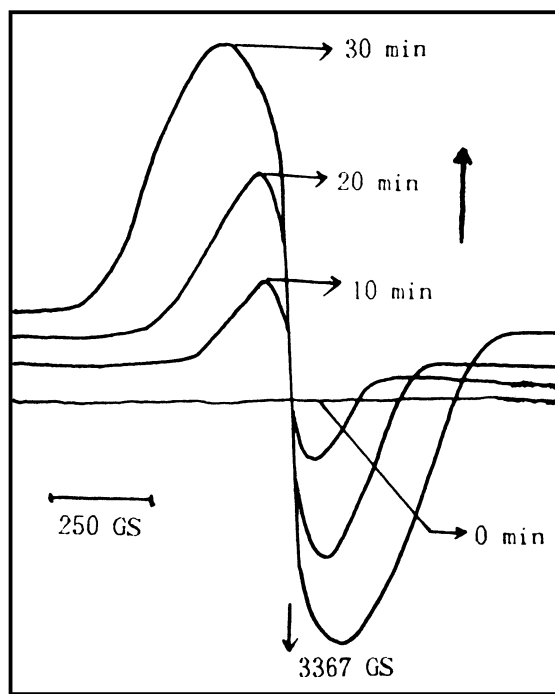


FIG. 8. ESR spectral change of $[\text{Fe}(\text{Qx})_3]^{3+}$ (2×10^{-4} mol/liter) + H_2O_2 (2×10^{-4} mol/liter) + H_2O system.

produce catechol and hydroquinone (28, 29). No resorcinol was detected in the phenol hydroxylation. Steps 4 and 5 are side reactions for diphenol production; the quantities of the by-products O_2 and benzoquinone change under different reaction conditions. By choosing suitable reaction conditions, good results can be obtained for phenol hydroxylation.

Table 2 shows that phenol hydroxylation proceeds better in water than in acetonitrile, acetone, and cyclohexane. The reason may be that phenol and H_2O_2 can reach the active sites more easily in water than in the organic solvents. In this way, the active species $\cdot OH$ is produced (step 1) and dispersed more easily, which could accelerate step 2. In cyclohexane, no reaction occurred; this may be due to the fact that no H_2O_2 could be dissolved in this solvent. In acetonitrile and acetone, it was also observed that hydroquinone instead of catechol was further oxidized (Table 2). It can also be confirmed with the following study that hydroquinone is more easily oxidized than catechol. In the hydroquinone + catechol + $[Fe(Qx)]_3^{2+} + H_2O_2 + H_2O$ reaction system, the concentration changes of some substances are shown in Fig. 10. Figure 10 also shows that hydroquinone can be easily further oxidized to benzoquinone through step 5; however, catechol cannot.

The pH value of the reaction medium has a great effect on phenol hydroxylation. When phenol hydroxylation was carried out in a weak acid medium, the average turnover frequency was higher than that in neutral and basic media

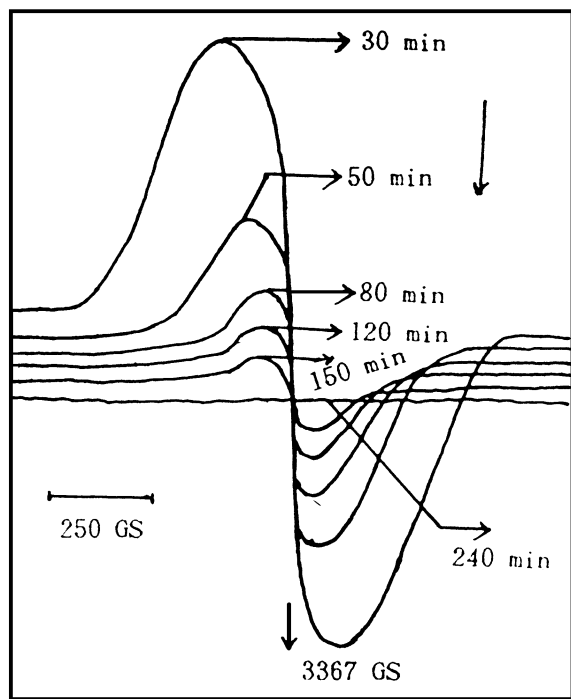
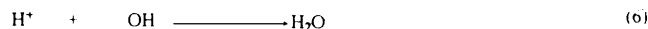
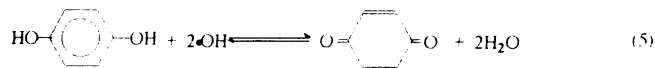
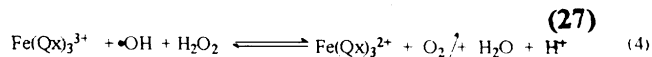
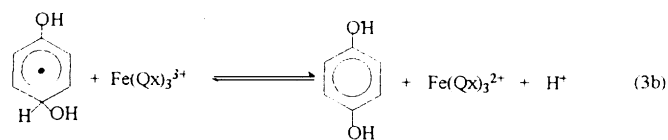
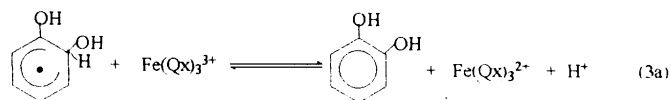
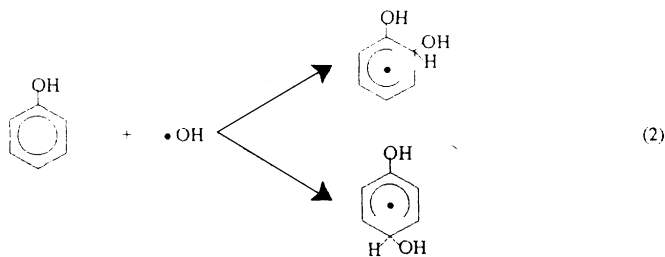
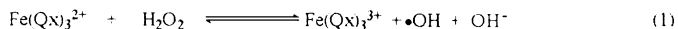


FIG. 9. ESR spectral change of the system described in Fig. 8 when phenol (4×10^{-4} mol/liter) is added to this system at 30 min.



SCHEME 1. Mechanism of the phenol hydroxylation catalyzed by iron(II)-8-quinolinol and iron(II)-8-quinolinol/MCM-41. $Qx = 8$ -quinolinol.

(Table 3). One reason might be that in the acidic reaction system, H^+ can accelerate step 1, thus producing more $\cdot OH$ than in the neutral and basic reaction systems. Another reason for the higher average turnover frequency in acidic medium may be due to the acid-catalyzed hydroxylation not involving radicals; however, when the pH was too low (e.g., pH 1), catalytic activity would decrease (Table 3), possibly because step 3 was greatly inhibited by H^+ . For the reaction in basic medium, the poor activity might have two causes: (1) Step 1 is inhibited by OH^- ; not enough $\cdot OH$ active species are produced for further reaction. (2) In basic medium, $Fe(Qx)_3^{3+}$ has poor oxidizability, which makes it difficult for $Fe(Qx)_3^{3+}$ to get electrons from the delocalized cyclohexadienyl radicals to produce catechol and hydroquinone (step 3).

CONCLUSION

The experiments show that MCM-41 is a good catalyst support for $[Fe(Qx)_3]Cl_2$. The good immobilization could

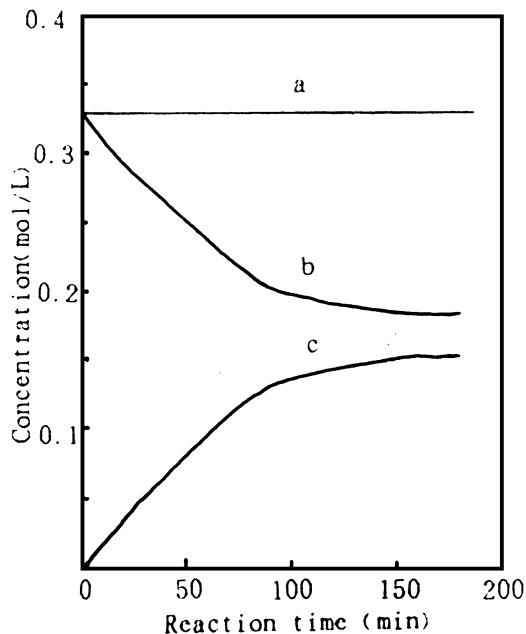


FIG. 10. Concentration change of catechol (a), hydroquinone (b), and benzoquinone (c). Reaction conditions: medium, water; pH 7.0; 50°C; time, 6 h; volume of reaction mixture, 15 ml; catechol = hydroquinone = 5×10^{-3} mol; molar ratio: catechol = hydroquinone/ H_2O_2 /catalyst (molarity of the support complex) = 1000/1000/1.

be due to the adsorption and static coulombic function between the pore wall of MCM-41 and $[\text{Fe}(\text{Qx})_3]^{2+}$ species. Iron(II)-8-quinolinol/MCM-41 has better catalytic activity than iron(II)-8-quinolinol and Fe^{2+} (Fenton agent). The better catalytic activity of the support iron(II)-8-quinolinol/MCM-41 might be attributed to the higher concentration of catalyst and substrates in the channels of MCM-41 and the distortion of iron(II)-8-quinolinol by the pore wall of MCM-41.

Moreover, the channels are large enough not only to allow phenol and H_2O_2 to approach catalytic centers freely, but also to allow products to move out easily. In this way, we could solve the problems caused by the limited pore sizes of microporous zeolite-encapsulated metal complexes. It might be possible for the larger ligand metal complexes to be immobilized in the channel and for a large substrate to enter the pore freely.

The successful hydroxylation of phenol and better activity compared with TS-1 (Table 1) demonstrated here mean that we can establish a new route for diphenol production.

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