

Photooxidation of benzene to phenol by ruthenium bipyridine complexes grafted on mesoporous silica FSM-16

Keiko Fujishima^a, Atsushi Fukuoka^a, Akihiko Yamagishi^b, Shinji Inagaki^c,
Yoshiaki Fukushima^c, Masaru Ichikawa^{a,*}

^a Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

^b Department of Biological Science, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

^c Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

Received 27 July 2000; received in revised form 18 August 2000; accepted 18 August 2000

Abstract

Catalytic performances of *bis*- and *tris*(bipyridine) Ru complexes grafted on mesoporous FSM-16 were studied in the photooxidation of benzene to phenol using H₂O₂ as an oxidant. [Ru(bpy)₃]Cl₂/FSM-16 showed a high activity under UV-irradiation, and the turnover number (TON) of phenol was 430 based on Ru in 24 h, and the selectivity to phenol among the products was 98%. Non-grafted [Ru(bpy)₃]Cl₂ complex gave a phenol TON of 170, thus demonstrating the promotion effect of grafting [Ru(bpy)₃]Cl₂ on FSM-16. The hydroxylation of benzene to phenol by [Ru(bpy)₃]Cl₂/FSM-16 slightly occurred in the dark (TON = 34 in 24 h), but the irradiation remarkably increased the TON of phenol by a factor of 13. The absorption peak of [Ru(bpy)₃]Cl₂ in the UV–VIS spectroscopy decreased under the reaction conditions; however, the recovered catalyst showed almost the same activity for phenol formation in the repeated runs. It is proposed that coordinatively unsaturated [Ru(bpy)_n]²⁺ (*n* = 1, 2) are generated by the UV-irradiation to [Ru(bpy)₃]Cl₂ on FSM-16. These species activate H₂O₂ to give an OH radical that attacks benzene as in the Fenton-type mechanism. Grafting of the Ru complex on FSM-16 may enhance the reaction of a hydroxycyclohexadienyl radical with the isolated Ru center. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photooxidation; Benzene; Phenol; Ru complex; FSM-16

1. Introduction

Direct and selective hydroxylation of benzene to phenol is currently one of difficult and challenging goals in heterogeneous and homogeneous catalyses as a potentially alternative route of the cumene process [1–7]. The Fenton's reagent method, which uses hydrogen peroxide as an oxidant, is widely studied in the direct oxidation of benzene [8–15]. The reaction

mechanism of the Fenton method has been proposed as follows; H₂O₂ reacts with Fe²⁺ (or other metal ions) to give a hydroxyl radical and Fe³⁺, and the hydroxyl radical attacks benzene to produce a hydroxycyclohexadienyl radical. Then the hydroxycyclohexadienyl radical is oxidized by Fe³⁺ to form phenol and Fe²⁺. The Fenton method is frequently accompanied by the formation of by-products such as biphenyl and further oxidation compounds of phenol. Biphenyl is formed by coupling of hydroxycyclohexadienyl radicals and subsequent dehydration, while catechol, hydroquinone and *p*-benzoquinone by further oxidation of phenol.

* Corresponding author. Tel.: +81-11-706-2912;
fax: +81-11-706-4957.
E-mail address: michi@cat.hines.hokudai.ac.jp (M. Ichikawa).

Ruthenium complexes having polypyridine ligands are intensively studied in artificial photosynthesis. In most cases, the Ru complexes are used as a photosensitizer to transmit the light energy to other catalysts or substrates [16–18]. However, the catalytic reactions promoted by $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ ($\text{bpy} = 2,2'$ -bipyridine) have been limitedly studied [19,20].

We have reported the “ship-in-bottle” synthesis of metal phthalocyanines in NaY zeolites which exhibit high regioselectivity in catalytic oxidation of *n*-hexane and hydrogenation of butadiene due to the isolated active species in micropores of NaY [21,22]. Recently, the “ship-in-bottle” approach is extended to mesoporous silicas such as FSM-16 and MCM-41, and we have shown the preparation of hybrid composites of metalloporphyrins [23], metal clusters [24], and fullerenes [25] in mesoporous FSM-16 and their catalytic activity in photooxidation of alkene and benzene. In this work, Ru complexes having bipyridine and chloride ligands such as $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, and RuCl_3 are grafted on mesoporous FSM-16, and their catalytic performances are investigated in liquid-phase photooxidation of benzene to phenol. A part of this work was preliminarily reported [26].

2. Experimental

2.1. Catalyst preparation

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (Aldrich), $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (Aldrich) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Wako) were used as received. FSM-16 (channel diameter 2.7 nm) was prepared according to the literature method [27]. Benzene (Wako, GR grade) and hydrogen peroxide (32% aqueous, Mitsubishi Gas Chemical, GR grade) were used without further purification.

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, and RuCl_3 were grafted on FSM-16 by the impregnation method (Fig. 1). Typically, FSM-16 (3.00 g) was evacuated at 623 K and 10^{-3} Torr for 2 h, and to the pretreated FSM-16 was added a solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (30.0 mg, 4.01×10^{-5} mol) in distilled water (30 ml) under N_2 . The mixture was vigorously stirred for 4 h. Then the mixture was evaporated to dryness and was dried at 10^{-3} Torr at room temperature for 12 h. $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were similarly impregnated on FSM-16, but methanol was used as a solvent for $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ due to its low solubility in water.

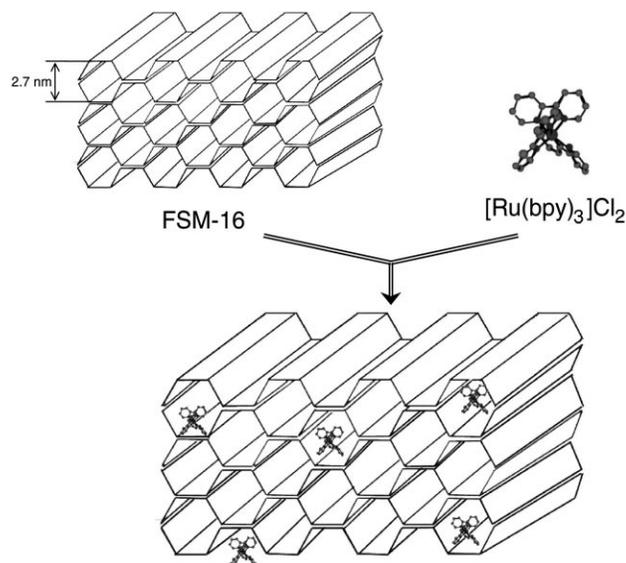


Fig. 1. Grafting of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ on FSM-16.

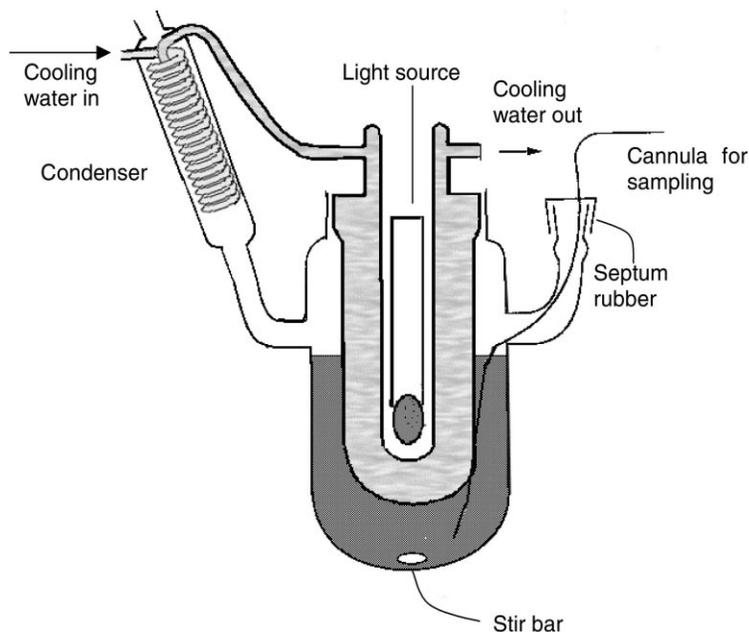


Fig. 2. A quartz reactor for photochemistry.

2.2. Catalytic reaction

Photooxidation of benzene was performed in a quartz reactor for photochemistry (Fig. 2), and a high-pressure mercury lamp (USHIO UM-102, 100 W, 250–600 nm) was used as a light source.

A mixture of benzene (75.0 ml, 840 mmol) and aq. H_2O_2 (32%, 75.0 ml, 710 mmol) was stirred with a heterogeneous or homogeneous catalyst (containing 5.7×10^{-3} mmol of Ru) under the photoirradiation at 300 K. A small portion of reaction mixture (500 μl) was periodically sampled from the reactor, and products were quantitatively analyzed by GC (Shimadzu GC-14B, column: J&W Scientific DB-WAX 0.25 mm \times 30 m), GC-MS (Perkin Elmer Q-Mass 910, column: J&W Scientific DB-WAX 0.25 mm \times 30 m) and HPLC (Shimadzu LC-10A, column: Waters μ -Bondasphere 5 m- C_{18} 100 \AA , 3.9 mm \times 150 mm).

In the reactions by RuCl_3 , $\text{RuCl}_3/\text{FSM-16}$, and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]/\text{FSM-16}$, brown solid was observed as a by-product. After filtration the solid was washed with benzene and distilled water, and was dried under vacuum at room temperature. FT-IR (Shimadzu FTIR-8100M spectrophotometer, KBr, cm^{-1}) gave

peaks at 3400 ($\nu(\text{O-H})$), 2920 and 2870 ($\nu(\text{C-H})$), 1740 ($\nu(\text{C=O})$), 1600 ($\nu(\text{C=C})$), 1200 and 1100 ($\nu(\text{C-O})$), which were ascribed to further oxidation products of phenol (vide infra).

In the experiment of the activity-dependence on the wavelength of UV-light, an ultrahigh-pressure mercury lamp (USHIO USH-500D, 500 W, 250–600 nm) and color glass cut-off filters (Toshiba L-39S: 390–800 nm and UV-D33S: 260–400 nm) were used.

2.3. Catalyst characterization

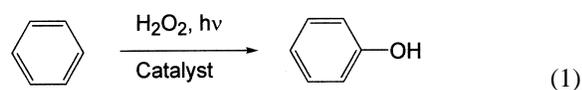
We studied the spectral change of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ complex under the conditions of catalytic reactions, and for this purpose the solution of non-grafted $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ complex was used because of the difficulty in following the UV-VIS spectral change of the powdered $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ catalyst. In order to evaluate the amount of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ dissolved in the lower water layer of the reaction mixture, UV-VIS spectra were acquired on a Shimadzu UV-2200A spectrophotometer using a quartz cell for liquid samples. A portion of water layer (50 μl) was sampled and was diluted in water to 0.50 ml of total volume

for the UV–VIS spectroscopy. On the other hand, in diffuse-reflectance UV–VIS spectroscopy, Ru complexes grafted on FSM-16 gave similar spectra to those of complexes in solutions in the transmission mode.

3. Results and discussion

3.1. Catalytic hydroxylation of benzene to phenol

Various Ru complexes having bpy and/or Cl ligands were grafted on FSM-16, and their catalytic performances were tested in the photooxidation of benzene (Eq. (1)). The results are summarized in Table 1.



By comparing the catalytic activities of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, and RuCl_3 on FSM-16, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ grafted on FSM-16 exhibited the highest TON (430) of phenol in 24 h under photoirradiation (Table 1, Run 1). Other minor product detected in this run was *p*-benzoquinone (TON = 6), thus giving phenol selectivity of 98% among the products. The TONs for bis(bpy) complex $[\text{Ru}(\text{bpy})_2\text{Cl}_2]/\text{FSM-16}$ and $\text{RuCl}_3/\text{FSM-16}$ were lower than that for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$: 280 and

360, respectively (Runs 2 and 3). In these cases, however, the TONs of *p*-benzoquinone were higher than that for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$. Furthermore, in the reactions by RuCl_3 , $\text{RuCl}_3/\text{FSM-16}$, and $[\text{Ru}(\text{bpy})_2\text{Cl}_2]/\text{FSM-16}$, brown solid was observed as a by-product (Runs 2, 3, 7 and 10). The solids were preliminarily assigned to oligomers or polymers of phenol and/or *p*-benzoquinone from their IR spectra (see Section 2). Therefore, the selectivities to phenol for $[\text{Ru}(\text{bpy})_2\text{Cl}_2]/\text{FSM-16}$ and $\text{RuCl}_3/\text{FSM-16}$ were lower than that for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$. No leaching of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ from FSM-16 to the solution phase was observed after the catalytic runs. When FSM-16 was used as a control run, H_2O_2 was vigorously decomposed to evolve O_2 but no oxidation of benzene was observed under the irradiation.

From Runs 1–3 in Table 1, it is suggested that bipyridine ligands have a role to reduce further oxidation of phenol to *p*-benzoquinone and to the brown solid. Substantial decomposition of H_2O_2 was also observed for $[\text{Ru}(\text{bpy})_2\text{Cl}_2]/\text{FSM-16}$ (H_2O_2 conversion 79%) and $\text{RuCl}_3/\text{FSM-16}$ (89%). On the other hand, the decomposition of H_2O_2 was decreased for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ (23%). The addition of excess bpy to $\text{RuCl}_3/\text{FSM-16}$ or $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ decreased the TON of phenol, but the formation of *p*-benzoquinone and solid by-product was effectively suppressed (Table 1, Runs 4 and 5).

Non-grafted $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ complex was also used as a catalyst, and the TON of phenol was 170

Table 1
Photooxidation of benzene to phenol by Ru catalysts with H_2O_2 ^a

Run	Catalyst	TON/Ru		Brown solid ^b (mg)
		Phenol	<i>p</i> -Benzoquinone	
1	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$	430	6	0
2	$[\text{Ru}(\text{bpy})_2\text{Cl}_2]/\text{FSM-16}$	280	48	9
3	$\text{RuCl}_3/\text{FSM-16}$	360	20	25
4	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16} + 13 \text{ bpy}$	74	7	0
5	$\text{RuCl}_3/\text{FSM-16} + 10 \text{ bpy}$	180	8	0
6	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	170	3	0
7	RuCl_3	83	8	20
8 ^c	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	0	0	0
9 ^c	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$	34	8	0
10 ^c	$\text{RuCl}_3/\text{FSM-16}$	260	41	30

^a Reaction conditions: benzene 840 mmol, H_2O_2 710 mmol, $\text{Ru } 5.7 \times 10^{-3}$ mmol, 300 K, 24 h, high pressure Hg lamp (Ushio UM-102, 100 W, 250–600 nm).

^b Oligomer or polymer of phenol and/or *p*-benzoquinone (see text).

^c Reactions in the dark.

(Table 1, Run 6), which was significantly lower than that for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$. RuCl_3 also gave a lower TON of phenol than the grafted $\text{RuCl}_3/\text{FSM-16}$. These results unambiguously demonstrate that grafting Ru complexes on FSM-16 effectively promotes the catalytic activity, which may be due to the isolation of the active Ru complex generated in the reaction.

Catalytic reactions without irradiation were also performed, and under the dark conditions, no or slight amount of phenol was observed for non-grafted and grafted $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (Table 1, Runs 8 and 9). On the other hand, $\text{RuCl}_3/\text{FSM-16}$ gave a high TON of 260 (Run 10). However, the irradiation greatly enhanced the phenol production for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ catalysts. Fig. 3 shows the time-course of TON of phenol by $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ with or without UV–VIS light. When the UV–VIS light was on after 3 h of the reaction, the phenol formation was significantly enhanced, but the formation rate was again reduced at 6 h when the light was off. This suggests that a photoactivation of catalytic species is involved in the catalytic cycle of hydroxylation mechanism.

3.2. Mechanistic study

We measured the conversion of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in the photoreaction by the spectroscopic methods. In

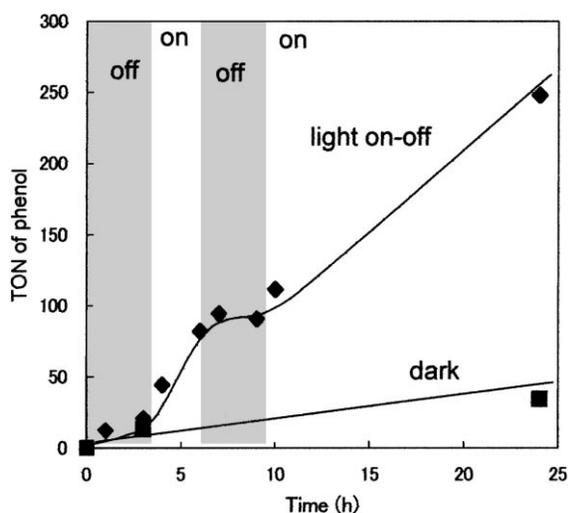


Fig. 3. Time-course of TON of phenol by $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ with or without the UV-irradiation. Conditions: see Run 1, Table 1.

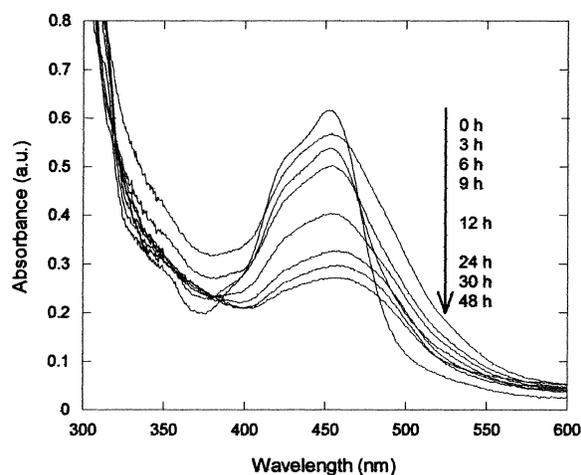


Fig. 4. UV–VIS spectral change of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in H_2O_2 under the UV-irradiation. Conditions: $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ 0.27 mmol, benzene 840 mmol, H_2O_2 710 mmol, Ru 5.7×10^{-3} mmol, high pressure Hg lamp (100 W, $\lambda = 250\text{--}600$ nm), 300 K.

the catalytic reaction by $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (e.g. Table 1, Run 6), the original orange color of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ turned to dark red. In UV–VIS spectroscopy of the reaction mixture, the peak at 453 nm due to MLCT [28] gradually decreased during the irradiation (Fig. 4), implying that the partial photosubstitution of the bpy ligand from Ru center. Without the photoirradiation, no spectral change was observed for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. The Ru complex was recovered after 24 h of irradiation by evaporating the solution. The resulting solid was characterized by UV–VIS and IR spectroscopies. The UV–VIS spectrum of the solid in water gave peaks at 242, 255, 287 and 458 nm in the region of 220–800 nm, indicating the presence of bpy ligand ($[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in water: 243, 248, 254, 280 and 453 nm). The IR spectrum of the solid also gave a band due to bpy ligand at 1400 cm^{-1} . In addition, strong broad bands were observed at 1590 ($\nu(\text{C}=\text{C})$) and $1150\text{--}1100$ ($\nu(\text{C}-\text{O})$) cm^{-1} , suggesting the presence of a phenoxo ligand. Therefore, we infer that the recovered solid contains bpy and OPh ligands. The recovered sample was used again as a catalyst. In this second catalytic run, a similar TON of phenol was obtained to that of the first catalytic run. This result indicates that $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ is converted to a catalytic active species having one or two bpy ligands under the UV–VIS irradiation, and that the resulting active species can be used in the repeated catalytic runs.

Table 2
Wavelength dependence of photocatalytic activity of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}^a$

Wavelength (nm)	TON/Ru	
	Phenol	<i>p</i> -Benzoquinone
250–400	100	2
390–600	41	2
250–600	96	4
Dark	15	0.4

^a Reaction conditions: benzene 840 mmol, H_2O_2 710 mmol, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ (Ru 5.7×10^{-3} mmol), 300 K, 9 h, ultrahigh pressure Hg lamp (Ushio USH-500D, 500 W, 250–600 nm).

The dependence of the catalytic activity of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ on wavelength was studied (Table 2). Irradiation of the light at 250–400 nm corresponds to the MC excitation of this complex [28], and the TON of phenol was 100, being almost the same as that for the irradiation at 250–600 nm. On the other hand, the TON of phenol was decreased from 96 to 41 at 390–600 nm of the MLCT excited range. It is known that the MC excited state of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ leads to the cleavage of Ru–N bond to give vacant sites at the Ru center (Fig. 5) [28]. From the wavelength dependence of the catalytic activity and the UV–VIS and IR spectra of the recovered catalyst from the reaction mixture, we suggest that coordinatively unsaturated $[\text{Ru}(\text{bpy})_n]^{2+}$ ($n = 1$ or 2) is formed by the dissociation of bpy from the photoexcited $[\text{Ru}(\text{bpy})_3]^{2+,*}$ species. The $[\text{Ru}(\text{bpy})_n]^{2+}$ species reacts with phenol as a product to give $[\text{Ru}(\text{bpy})_n(\text{OPh})_{6-2n}]$ ($n = 1$ or 2).

Although the mechanism of the photooxidation of benzene is not fully understood at this moment, we propose that the coordinatively unsaturated Ru(II) species, $[\text{Ru}(\text{bpy})_n]^{2+}$ ($n = 1$ or 2), promotes both the formation of OH radical from H_2O_2 and the attack of the OH radical to benzene as proposed for the Fenton reagent (Fig. 6) [8–15]. The reaction of $[\text{Ru}(\text{bpy})_n]^{2+}$ ($n = 1$ or 2) with H_2O_2 produces an OH radical and $[\text{Ru}(\text{bpy})_n]^{3+}$, and the OH radical attacks benzene to form a hydroxycyclohexadienyl ($\text{C}_6\text{H}_6\text{OH}$) radical. The oxidation of hydroxycyclohexadienyl radical by $[\text{Ru}(\text{bpy})_n]^{3+}$ results in the formation of phenol and regeneration of $[\text{Ru}(\text{bpy})_n]^{2+}$. In the typical Fenton reagent system, substantial formation of biphenyl is observed, which results from coupling of the hydroxycyclohexadienyl radical. However, the coupling is minor in the present photocatalytic reaction by $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$ as shown in Table 1. Therefore, the reduction from the hydroxycyclohexadienyl radical to phenol is faster than the coupling to biphenyl. By comparing the catalytic results of Ru precursors having different numbers of bpy and Cl ligands (Table 1, Runs 1–3), the bpy ligand on the Ru center retards further oxidation of phenol to *p*-benzoquinone and polymeric compounds. Moreover, grafting of complexes on FSM-16 substantially enhanced the catalytic activity (Table 1, Runs 1 and 3 versus 5 and 6) over the non-grafted complexes. From these results, we propose that the hydroxycyclohexadienyl radical is located near the coordination sphere of $[\text{Ru}(\text{bpy})_n]^{3+}$ in the mesopores of FSM-16, which

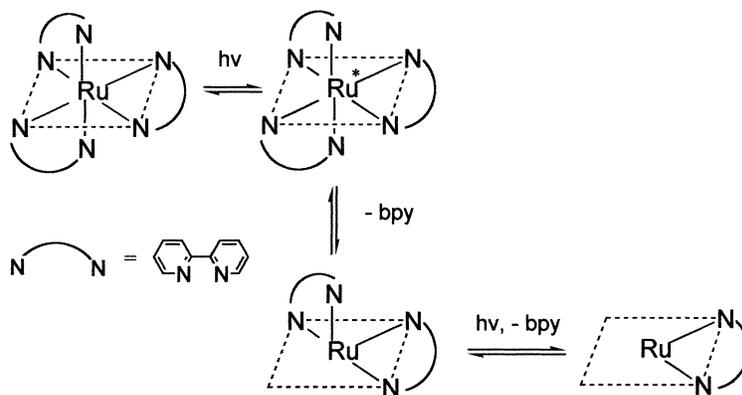


Fig. 5. Photosubstitution of bipyridine in the MC excitation of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$.

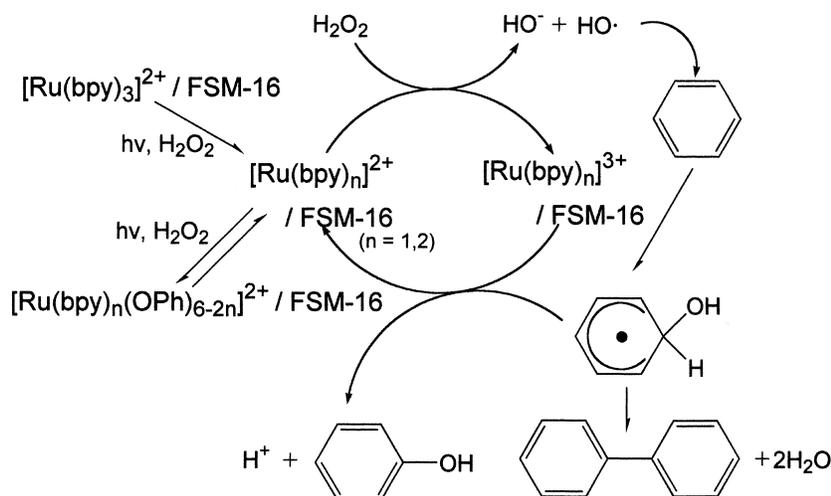


Fig. 6. Proposed reaction mechanism for the photooxidation of benzene by $[\text{Ru}(\text{bpy})_3]\text{Cl}_2/\text{FSM-16}$.

results in the facile reaction of the radical with the Ru(III) and the suppression of dimerization of the radical.

4. Conclusions

1. $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ grafted on mesoporous FSM-16 catalytically oxidizes benzene to produce phenol in high activity and selectivity using H_2O_2 as an oxidant under UV–VIS irradiation.
2. Grafting of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ on FSM-16 enhances the formation of phenol, possibly due to the site isolation of active Ru species.
3. Bipyridine ligands suppress the further oxidation of phenol.
4. The MC excitation of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in UV–VIS irradiation effectively increases the hydroxylation of benzene to phenol.
5. The MC excitation of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ results in the cleavage of Ru–N bonds to give coordinatively unsaturated $[\text{Ru}(\text{bpy})_n]^{2+}$ ($n = 1$ or 2), which activates H_2O_2 to produce OH radical in the Fenton-type mechanism.

Acknowledgements

This work was supported by the Proposal-based New Industry Creative Type Technology R&D Promo-

tion Program from the new energy and industrial technology development organization (NEDO) of Japan.

References

- [1] R.A. Sheldon, in: R.A. van Santen (Eds.), *Catalytic Oxidation — Principles and Applications*, World Scientific Publishing Co., Singapore, 1995.
- [2] G. Centi, M. Misono, *Catal. Today* 41 (1998) 287.
- [3] Y. Moro-oka, M. Akita, *Catal. Today* 41 (1998) 327.
- [4] S. Ito, A. Mitarai, K. Hikino, M. Hiramata, K. Sasaki, *J. Org. Chem.* 57 (1992) 6937.
- [5] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, *Nature* 368 (1994) 321.
- [6] T. Miyake, M. Hamada, Y. Sasaki, M. Oguri, *Appl. Catal. A* 131 (1995) 33.
- [7] I. Yamanaka, K. Morimoto, M. Soma, K. Otsuka, *J. Mol. Catal. A* 133 (1998) 251.
- [8] C. Walling, *Acc. Chem. Res.* 8 (1975) 125.
- [9] J.R.L. Smith, R.O.C. Norman, *J. Chem. Soc.* (1963) 2897.
- [10] C. Walling, R.A. Johnson, *J. Am. Chem. Soc.* 97 (1975) 363.
- [11] T. Tagawa, Y. Seo, S. Goto, *J. Mol. Catal.* 78 (1993) 201.
- [12] L.I. Kunznetsova, L.G. Detusheva, M.A. Fedotov, V.A. Likhonov, *J. Mol. Catal. A* 111 (1996) 81.
- [13] K. Nomiya, H. Yanakibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, Y. Shimizu, *J. Mol. Catal. A* 114 (1996) 181.
- [14] Y. Mao, A. Bakac, *Inorg. Chem.* 35 (1996) 3925.
- [15] X. Lu, N. Mizuno, M. Misono, *Nipponkagakuishi* (1998) 23.
- [16] E. Amouval, P. Keller, A. Moradfour, *J. Chem. Soc., Chem. Comm.* (1980) 1019.
- [17] H.A.F. Werner, R. Bauer, *J. Mol. Catal.* 88 (1994) 185.

- [18] M. Suzuki, S. Kobayashi, S. Uchida, M. Kimura, K. Hanabusa, H. Shirai, *Polymer* 39 (1997) 1539.
- [19] M. Fukushima, K. Tatsumi, S. Tanaka, H. Nakamura, *Environ. Sci. Technol.* 32 (1998) 3948.
- [20] T. Kojima, Y. Matsuda, For polypyridine Ru complex, *Chem. Lett.* (1999) 81.
- [21] T. Kimura, A. Fukuoka, M. Ichikawa, *Catal. Lett.* 4 (1990) 279.
- [22] M. Ichikawa, T. Kimura, A. Fukuoka, in: T. Inui, S. Nanba, T. Tatsumi (Eds.), *Chemistry of Microporous Crystals*, Elsevier, Amsterdam, 1991, p. 335.
- [23] J. Tachibana, M. Chiba, M. Ichikawa, T. Imamura, Y. Sasaki, *Supramol. Sci.* 5 (1998) 281.
- [24] K. Zama, A. Fukuoka, Y. Sasaki, S. Inagaki, Y. Fukushima, M. Ichikawa, *Catal. Lett.* 66 (2000) 251.
- [25] A. Fukuoka, K. Fujishima, M. Chiba, J. Tachibana, M. Ichikawa, *Catal. Lett.*, in press.
- [26] K. Fujishima, A. Fukuoka, M. Ichikawa, *Stud. Surf. Sci. Catal.* 130 (2000) 1979.
- [27] S. Inagaki, Y. Fukushima, K. Kuroda, *J. Chem. Soc., Chem. Comm.* (1993) 680.
- [28] A. Juris, V. Balzani, *Coord. Chem. Rev.* 84 (1988) 85.