



Oxidation of cyclic hydrocarbons with hydrogen peroxide over iron complexes encapsulated in cation-exchanged zeolite^{*}

Syuhei Yamaguchi^{*}, Yuki Miyake, Keiko Takiguchi, Daijiro Ihara, Hidenori Yahiro

Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan

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ABSTRACT

Fe-bipyridine complexes were encapsulated into cation-exchanged Y-type zeolites (M-Na-Y: M = K⁺, Cs⁺, Mg²⁺, Ca²⁺, NH₄⁺, TMA⁺, and TBA⁺) and their catalytic activities for oxidation of benzene with hydrogen peroxide (H₂O₂) to phenol were investigated in three types of solvents (CH₃CN, H₂O, and CH₃CN + H₂O(1:1)). Regardless of the kind of solvent, the counter cation in [Fe(bpy)₃]²⁺@M-Na-Y did not affect the selectivity to phenol. No significant difference in catalytic activity of [Fe(bpy)₃]²⁺@M-Na-Y appeared in CH₃CN + H₂O (1:1), while a difference on catalytic activity appeared in each CH₃CN and H₂O solvent. It was suggested that the catalytic activity is related with the accessibility of benzene to [Fe(bpy)₃]²⁺ site in [Fe(bpy)₃]²⁺@M-Na-Y, controlled by the hydrated ionic radius of the counter cation introduced. The effect of ligand coordinated with Fe ion was investigated by comparing the catalytic activities for oxidation of cyclic hydrocarbons (benzene, cyclohexane, and cyclohexene) over [Fe(bpy)₃]²⁺@Na-Y, [Fe(phen)₃]²⁺@Na-Y, and [Fe(terpy)₂]²⁺@Na-Y (phen = 1,10-phenanthroline and terpy = 2,2',6',2''-terpyridine). It was suggested that the expansion of π-electron over the ligands such as phen and terpy improves the uptake ability of substrates having π-electron such as benzene.

1. Introduction

The direct hydroxylation of hydrocarbons is one of the highly difficult oxidation reactions and is also very important from the viewpoint of the development of green chemistry procedures and environmental friendly technologies to keep sustainable growth. The selective oxidation of hydrocarbons is still a challenge in chemical industries and academic fields. Especially, the catalytic hydroxylation of benzene to phenol with environment-friendly oxidants, such as hydrogen peroxide (H₂O₂) [1–9], N₂O [10–13], O₂ in combination with reducing agents [1,14–20], and H₂O with electrochemical [21] or photochemical reaction systems [22,23] has attracted much attention.

One of the most attractive areas in catalysis is the development of inorganic-organic hybrid materials active for oxidation reactions [24–28]. Many researchers have reported the oxidation of organic substrates (benzene [9,29], phenol [30,31], cyclohexane [25,32], cyclohexene [25,33], sulfides [34], and others [24,26–28]) with H₂O₂ as an oxidant over transition metal complexes encapsulated in Y-type zeolite. Mori et al. reported the preparation of [Fe(bpy)₃]²⁺@M-Na-Y catalysts (M = alkali metal ions (Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺) [9], and alkaline earth metal ions (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) [35]) and their

applications for photochemical and oxidation reactions in organic solvents. Recently, we reported the catalytic activity of [Fe(bpy)₃]²⁺@Na-Y catalyst for oxidation of benzene and cyclohexene with H₂O₂ in CH₃CN and/or H₂O solvent [36–38]. [Fe(bpy)₃]²⁺@Na-Y catalyst exhibited high selectivity for oxidation of cyclohexene with H₂O₂ to cyclohexen-1-ol [37,38]. The catalytic activity of [Fe(bpy)₃]²⁺@Na-Y for oxidation of benzene increased with increasing the amount of H₂O added to CH₃CN solvent. Maximum value of catalytic activity was obtained when the volume ratio of the solvents was equal (CH₃CN:H₂O = 1:1) [36]. In this report, the preparation of Fe-bipyridine complexes encapsulated into cation-exchanged zeolites ([Fe(bpy)₃]²⁺@M-Na-Y catalysts (M = K⁺, Cs⁺, Mg²⁺, Ca²⁺, NH₄⁺, TMA⁺, and TBA⁺)) and their catalytic activities for oxidation of benzene with H₂O₂ in CH₃CN and/or H₂O were investigated to clarify the effect of the counter cation located in zeolite (Scheme S1 (1)). Furthermore, Fe-L complexes with different ligands, L = 1,10-phenanthroline (phen) and 2,2',6',2''-terpyridine (terpy) were prepared into Y-type zeolite ([Fe(phen)₃]²⁺@Na-Y and [Fe(terpy)₂]²⁺@Na-Y, respectively) and their catalytic activities for oxidation of cyclic hydrocarbons such as benzene, cyclohexane, and cyclohexene with H₂O₂ were investigated to clarify the effect of ligand in catalysts (Scheme S1 (2)).

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^{*} Corresponding author.

E-mail address: syuhei@ehime-u.ac.jp (S. Yamaguchi).

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2. Experimental

2.1. Materials and instruments

Na ion-exchanged Y-type zeolite (Na-Y) with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.5$ was supplied from Tosoh Co. The following chemicals were used as received: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Wako, > 99%), sodium nitrate (Wako, 99.0%), potassium nitrate (Wako, 99.0%), cesium nitrate (Wako, 99.0%), magnesium nitrate (Wako, 99.0%), calcium nitrate (Wako, 99.0%), ammonium nitrate (Wako, 99.0%), tetramethylammonium nitrate (Wako, 99.0%), tetra-*n*-butylammonium nitrate (Wako, 99.0%), 2,2'-bipyridine (Wako, 99.5%), 1,10-phenanthroline (Nacalai, 99%), 2,2';6',2''-terpyridine (TCI, 98.0%), methanol (Wako, 99.8%), 30% aqueous hydrogen peroxide (Wako, 30–35.5%), benzene (Wako, 99.5%), phenol (Wako, 99.0%), catechol (Wako, 99.0%), hydroquinone (Wako, 99.0%), cyclohexene (Wako, 97.0%), cyclohexene oxide (TCL, > 98%), 2-cyclohexen-1-ol (ALDRICH, 95%), 2-cyclohexen-1-one (Wako, 95%), mixture of *cis* and *trans*-1,2-cyclohexanediols (Alfa Aesar, 98%), *cis*-1,2-cyclohexanediol (Wako), cyclohexane (Wako, 99.0%), cyclohexanol (Wako, 99.0%), cyclohexanone (Wako, 99.0%), *o*-dichlorobenzene (Wako, 98.0%), and acetonitrile (Wako, 99.5%). Cyclohexene was used as a substrate after purification with treatment of activated alumina and distillation to remove peroxide and oxidative species derived from cyclohexene.

ICP-AES and CHN elemental analyses of all the catalysts were carried out after the sample was dissolved into HF solution (Table 1 and Table S1). The powder XRD patterns of catalysts were collected on a Rigaku MiniFlex II diffractometer using $\text{CuK}\alpha$ radiation. UV–vis. spectra were recorded on a Hitachi U-4000 spectrometer for solid samples or on Shimadzu U-1200 for liquid samples. GC analysis was performed on Shimadzu GC-2014 with a flame ionization detector equipped with a DB-1MS capillary column (internal diameter = 0.25 mm and length = 30 m) at the nature of non-polar liquid phase.

2.2. Sample preparation

Na^+ ions existing as counter cations of Y-type zeolite (Na-Y) were partially ion-exchanged with aqueous solutions containing $\text{M} = \text{K}^+$, Cs^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , TMA^+ , and TBA^+ (nitrate) at room temperature to yield M-Na-Y zeolite. Na-Y and M-Na-Y zeolites (2.5 g) were ion-exchanged by a conventional method using aqueous solution (150 mL) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.1 g, 0.36 mmol) to yield iron(II) ion-exchanged Y-type zeolite (Fe-Na-Y and Fe-M-Na-Y). The prepared Fe-Na-Y (1.0 g) was refluxed in an aqueous solution (100 mL) of 2,2'-bipyridine

Table 1
Elemental analysis of Fe complexes encapsulated in cation-exchanged zeolite.

Catalyst	Degree of exchange/% ^a		
	Na	M ^b	Fe
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{Na-Y}$	82	–	11
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{K-Na-Y}$	23	56	10
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{Cs-Na-Y}$	41	57	11
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{Mg-Na-Y}$	29	59	9.6
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{Ca-Na-Y}$	64	23	11
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{NH}_4\text{-Na-Y}$	35	43 ^c	11
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{TMA-Na-Y}$	76	27 ^c	12
$[\text{Fe}(\text{bpy})_3]^{2+}@\text{TBA-Na-Y}$	98	5 ^c	12
$[\text{Fe}(\text{phen})_3]^{2+}@\text{Na-Y}$	85	–	11
$[\text{Fe}(\text{terpy})_2]^{2+}@\text{Na-Y}$	74	–	11

^a Degree of exchange [%] = valence \times each of the cation [mol] \times Al [mol] \times 100.

^b Exchanged cation of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Na-Y}$ ($\text{M} = \text{K}^+$, Cs^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , TMA^+ , and TBA^+).

^c Degree of exchange of each alkyl ammonium cation was estimated from CHN analysis and TG-DTA results.

(bpy) (0.47 g, 3.0 mmol) for 20 h, followed by filtration, washing with water and methanol by Soxhlet extractor, and drying at room temperature under vacuum to give $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Na-Y}$ as a reddish-pink powder. In a similar way, $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Na-Y}$ samples ($\text{M} = \text{K}^+$, Cs^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , TMA^+ , and TBA^+) were prepared by using Fe-M-Na-Y. $[\text{Fe}(\text{phen})_3]^{2+}@\text{Na-Y}$ and $[\text{Fe}(\text{terpy})_2]^{2+}@\text{Na-Y}$ were prepared by reacting Fe-Na-Y with 1,10-phenanthroline (phen) and 2,2';6',2''-terpyridine (terpy), giving orange and purple powders, respectively.

2.3. Catalytic oxidation

The catalytic oxidations of benzene, cyclohexane, and cyclohexene were carried out with a glass tube reactor. A typical procedure was as follows; catalyst (7.9 μmol), MeCN and/or H_2O solvent (10 mL), and substrate (7.9 mmol) were charged, and 30% aqueous hydrogen peroxide (0.8 or 7.9 mmol) was added in glass tube reactor under Ar atmosphere. The reaction was carried out at 50 °C. After the reaction, triphenylphosphine as a quencher and *o*-dichlorobenzene as an internal standard were added into glass tube reactor. The reaction solution was analyzed by GC in combination with a flame ionization detector (FID). The products were identified by the comparison of mass spectra with those authentic samples.

3. Results and discussion

3.1. Characterization of catalysts

The characterization of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Na-Y}$ has been already reported by a few researchers [9,39–41] and us [37] in detail. $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Na-Y}$ ($\text{M} = \text{K}^+$, Cs^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , TMA^+ , and TBA^+), $[\text{Fe}(\text{phen})_3]^{2+}@\text{Na-Y}$, and $[\text{Fe}(\text{terpy})_2]^{2+}@\text{Na-Y}$ were prepared and characterized in this study. The elemental analysis shown in Table 1 indicated that Fe ion in zeolite Y was coordinated with three bpy (bpy/Fe = 3), three phen (phen/Fe = 3), and two terpy (terpy/Fe = 2) ligands, suggesting the formation of $[\text{Fe}(\text{bpy})_3]^{2+}$, $[\text{Fe}(\text{phen})_3]^{2+}$, and $[\text{Fe}(\text{terpy})_2]^{2+}$ ions, respectively. The sum of exchange degrees of Na, M, and Fe was in the range from 88% to 115% for all the catalysts. The slight deviation from 100% may come from the following possibilities. One possibility is that the protons are partially exchanged during the synthesis of catalysts. The other possibility is that the Na and Fe contents are excessively estimated by increasing the base lines of ICP-AES results derived from chemical interference of organic compounds, such as ligands and organic cations.

XRD patterns of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Na-Y}$ ($\text{M} = \text{Na}^+$, K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , TMA^+ , and TBA^+), $[\text{Fe}(\text{phen})_3]^{2+}@\text{Na-Y}$, $[\text{Fe}(\text{terpy})_2]^{2+}@\text{Na-Y}$, and Na-Fe-Y are shown in Fig. 1. This figure demonstrates that the zeolite structure has kept even after the introduction of each metal complex. It has been reported that the empirically derived relationship between the relative peak intensities of the (220) and (311) reflections in the XRD pattern confirms the formation of a large metal ion in a supercage of faujasite-type zeolite; the intensity of (220) for the zeolite containing large complexes is lower than that for the original zeolite Y, while the intensity of (311) for former is greater than that for the latter [9,37,39–41]. As can be seen in Fig. 1(a)–(i), S1, and S2, the intensities of (220) ($2\theta = 10$) for $[\text{Fe}(\text{bpy})_3]^{2+}@\text{M-Na-Y}$ ($\text{M} = \text{Na}^+$, K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , TMA^+ , and TBA^+) were lower than those for the corresponding Fe-M-Na-Y samples, while the intensities of (311) ($2\theta = 12$) for former ones were greater than those for latter ones. Similar results were obtained for $[\text{Fe}(\text{phen})_3]^{2+}@\text{Na-Y}$ and $[\text{Fe}(\text{terpy})_2]^{2+}@\text{Na-Y}$ catalysts (Fig. 1(j), (k), and S3). These are clear evidences for the formation of metal complex ions within the supercage.

UV–vis. diffuse reflectance spectra of $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Na-Y}$, $[\text{Fe}(\text{phen})_3]^{2+}@\text{Na-Y}$, $[\text{Fe}(\text{terpy})_2]^{2+}@\text{Na-Y}$, Fe-Na-Y, and Na-Y are shown in Fig. 2. No absorption was observed from the ultraviolet to

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