

Selective Hydroxylation of Cyclohexene in Water as an Environment-friendly Solvent with Hydrogen Peroxide over Fe-Bipyridine Encapsulated in Y-type Zeolite

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The selective hydroxylation of cyclohexene to 2-cyclohexen-1-ol with hydrogen peroxide in water was successfully achieved using $[\text{Fe}(\text{bpy})_3]^{2+}$ complexes encapsulated into Y-type zeolite.

Recently, government projects and new legislation demand large investment in green chemistry procedures and environmentally friendly technologies. One of the most interesting areas in catalysis is the development of inorganic-organic hybrid materials for catalytic oxidation reactions.¹⁻³ The selective oxidation of hydrocarbons is still a challenge in chemical industries and academic fields. As a test reaction for catalytic activity, the oxidation of cyclohexene with hydrogen peroxide using homogeneous Fe complexes has been reported by many researchers.^{4,5} Que et al. reported that cyclohexene oxide and cyclohexane diol were formed by the oxidation of cyclohexene with hydrogen peroxide using Fe complexes controlled by designed tetradeinate ligands.⁴ However, there is little information about the selective hydroxylation of cyclohexene with hydrogen peroxide using Fe complexes to 2-cyclohexen-1-ol, due to the subsequent oxidation of 2-cyclohexen-1-ol to 1-one.⁵ In recent years, the immobilization of transition-metal complexes on the surface of supports or the encapsulation of transition-metal complexes inside porous materials has received considerable attention. Such an application can result in a significant enhancement of novel catalytic activities that homogeneous catalysts have not exhibited yet.⁶⁻⁸ Utilizing water as an alternate to toxic and harmful organic solvents is important and has been extensively studied.⁹⁻¹⁴ Thus, the combination of catalysts with iron as a ubiquitous metal and water as a solvent seems to be very attractive from a viewpoint of green sustainable chemistry.¹⁵⁻¹⁷

The Y-type zeolite belonging to the faujasite family has large cavities, so-called supercages, with a diameter of ca. 13.0 Å.¹⁸ These supercages are connected to each other by tunnels or windows with a widest diameter of ca. 7.4 Å. The estimated diameter of $[\text{Fe}(\text{bpy})_3]^{2+}$ complex (ca. 12 Å) is larger than a window size of supercage so that the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex synthesized in supercage cannot go out from the cavity (Scheme S1¹⁹). Therefore, $[\text{Fe}(\text{bpy})_3]^{2+}$ complexes encapsulated into Na-Y ($[\text{Fe}(\text{bpy})_3]^{2+}$ @Y) have been reported as a heterogeneous oxidation catalyst.^{2,20-23} However, there is no information about the activity of $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y catalyst for selective oxidation with hydrogen peroxide as a oxidant in water solvent. In this report, $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y was characterized by several methods and solvent effects on its catalytic activity for oxidation of cyclohexene with hydrogen peroxide was investigated.

Fe ion-exchanged Y-type zeolite (Fe-Y) was prepared from Na-Y with FeSO_4 solution. $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y was obtained by

the reaction of Fe-Y with bipyridine (bpy) (Scheme S2).¹⁹ This compound was characterized by XRD, UV-vis., and elemental analysis. As a model reaction for evaluating the catalytic activity, the partial oxidation of cyclohexene was carried out. Each catalyst (7.9 μmol Fe atoms in catalysts), cyclohexene (7.9 mmol), 30% H_2O_2 (65 μL, 0.8 mmol), and solvent (acetone-nitrile (10 – x mL), water (x mL)) were stirred at 50 °C under Ar. The yield was determined periodically by GC analysis.

Elemental analysis of C, H, N, and Fe for $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y indicated that the ratio of bpy ligands/Fe ions was ca. 3 (Table S1¹⁹), suggesting that free and uncomplexed Fe(II) ions hardly remained. This result also suggests that approximately one $[\text{Fe}(\text{bpy})_3]^{2+}$ complex per two supercages in zeolite was contained in $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y.

It has been reported that the relationship between the relative peak intensities of the 220 (I_{220}) and 311 (I_{311}) reflections in the XRD pattern is closely related to the formation of a large metal complex ion in the supercage of faujasite-type zeolites: $I_{220} > I_{311}$ for the original Y-type zeolite and $I_{220} < I_{311}$ for the zeolite containing large complexes.^{2,20-24} As shown in Figure S1,¹⁹ I_{220} at $2\theta = 10^\circ$ was greater than I_{311} at 12° for Fe-Y, while I_{220} is lower than I_{311} for $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y. This is clear evidence for the formation of complex ions within the supercages.

Figure 1 shows UV-vis diffuse reflectance spectra of $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y, $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2 + \text{Na-Y}$, and Fe-Y. The absorption spectrum of $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2 + \text{Na-Y}$ gave three bands at 533 and 360 nm assigned to a metal-to-ligand (d–π*) charge-transfer (MLCT),²⁵⁻²⁷ and 295 nm assigned to a π–π* transition of the bpy ligand,²⁷ similar to that of $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ in CH_3CN (Figure S2).^{19,28} $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y exhibits

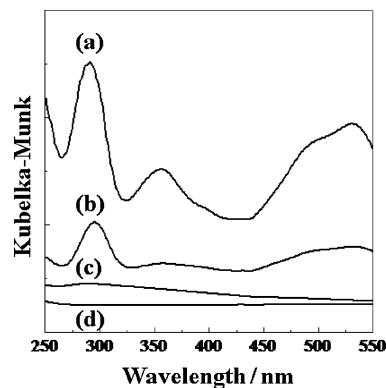


Figure 1. UV-vis diffuse reflectance spectra of (a) $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y, (b) $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2 + \text{Na-Y}$, (c) Fe-Y, and (d) Na-Y, where the amount of Fe contained in each sample was held constant except for Na-Y.

Table 1. Oxidation of cyclohexene with hydrogen peroxide over Fe-containing catalysts^a

Catalyst	Solvent	H ₂ O ₂ conv./%	Product/10 ⁻⁵ mol (Selectivity/%) ^b				H ₂ O ₂ efficiency /% ^c
			Cyclohexen-1-ol	Cyclohexen-1-one	Cyclohexene oxide	Others ^d	
[Fe(bpy) ₃] ²⁺ @Y	CH ₃ CN	58	27.4 (91)	2.1 (7)	0.6 (2)	0	66
[Fe(bpy) ₃](ClO ₄) ₂	CH ₃ CN	94	22.0 (58)	11.8 (31)	3.2 (9)	0.9 (2)	51
Fe-Y	CH ₃ CN	92	24.5 (91)	1.3 (5)	1.0 (4)	0	37
[Fe(bpy) ₃] ²⁺ @Y	H ₂ O	47	19.5 (>99)	0	0	0	53
[Fe(bpy) ₃](ClO ₄) ₂	H ₂ O	98	2.9 (25)	6.1 (52)	0	2.6 (22)	15
Fe-Y	H ₂ O	52	3.4 (>99)	0	0	0	8

^aReaction condition: Fe (7.9 μmol), cyclohexene (7.9 mmol), H₂O₂ (0.79 mmol), solvent (10 mL), 50 °C, 24 h under Ar. ^bSelectivity (%) = (product [mol])/(all products [mol]) × 100. ^cH₂O₂ efficiency (%) = (all products [mol])/(consumed H₂O₂ [mol]) × 100. ^dOthers: 1,2-cyclohexanediols (cis and trans) assigned with standard reagents.

similar MLCT band (531 nm) but a slight blue-shift of the π - π^* transition band at 290 nm. In spite of the same amount of [Fe(bpy)₃]²⁺, the intensity of the band assigned to π - π^* transition in [Fe(bpy)₃]²⁺@Y was larger than that in [Fe(bpy)₃](ClO₄)₂ + Na-Y, because the intermolecular π - π stacking interaction of bpy ligands as shown in crystal structures of [Fe(bpy)₃](ClO₄)₂ (Figure S3¹⁹) was inhibited by immobilization of complexes into supercages.²⁹ These results support that [Fe(bpy)₃]²⁺ complex ions exist within the supercages of zeolite Y.

Table 1 summarizes the catalytic activities of [Fe(bpy)₃]²⁺@Y and Fe-Y for the oxidation of cyclohexene with hydrogen peroxide in CH₃CN and H₂O solvents. The result of [Fe(bpy)₃](ClO₄)₂ as a homogeneous catalyst is also shown in this table. No catalytic activity for oxidation of cyclohexene with H₂O₂ was observed with Na-Y and without catalyst under the same experimental conditions. In the case of CH₃CN as an organic solvent, the product yield and the selectivity of 2-cyclohexen-1-ol generated on [Fe(bpy)₃]²⁺@Y were similar to those on Fe-Y. As can be seen in Table 1, the selectivity to 2-cyclohexen-1-ol for [Fe(bpy)₃]²⁺@Y- and Fe-Y-catalyzed oxidations of cyclohexene was ca. 90%, which was much higher than that for [Fe(bpy)₃](ClO₄)₂-catalyzed oxidation. Interestingly, [Fe(bpy)₃]²⁺@Y showed much higher H₂O₂ efficiency than [Fe(bpy)₃](ClO₄)₂ and Fe-Y. The recycle test of [Fe(bpy)₃]²⁺@Y in CH₃CN demonstrated no degradation of either the catalytic activity or selectivity to 2-cyclohexen-1-ol during at least three runs (Table S2;¹⁹ after the first reaction, the catalyst was filtered, washed with CH₃CN three times, dried under air, and supplied to the next catalytic run).

Figure 2 shows the effect of H₂O addition to CH₃CN solvent with [Fe(bpy)₃]²⁺@Y and [Fe(bpy)₃](ClO₄)₂ catalysts. When water was added into CH₃CN solvent, the product yield of 2-cyclohexen-1-ol with [Fe(bpy)₃](ClO₄)₂ gradually decreased with increasing the amount of water added (Figure 2b), while the products yields with [Fe(bpy)₃]²⁺@Y hardly decreased (Figure 2a). As can be seen in Table 1, the product yield of 2-cyclohexen-1-ol over [Fe(bpy)₃]²⁺@Y in water solvent (x = 10 mL) was about five times larger than that over [Fe(bpy)₃](ClO₄)₂. [Fe(bpy)₃](ClO₄)₂ as homogeneous catalyst showed higher H₂O₂ conversion than the other tested Fe catalysts, although it exhibited much lower H₂O₂ efficiency

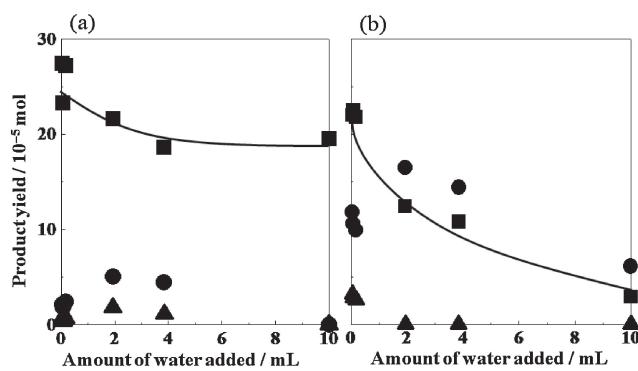


Figure 2. Effect of water addition into solvent for catalytic activity of (a) [Fe(bpy)₃]²⁺@Y and (b) [Fe(bpy)₃](ClO₄)₂ (□; 2-cyclohexen-1-ol, ●; 2-cyclohexen-1-one, ▲; cyclohexene-oxide). Reaction conditions: Fe in catalysts (7.9 μmol), cyclohexene (7.9 mmol), 30% aqueous H₂O₂ (0.8 mmol), solvent (total 10 mL; CH₃CN (10 - x mL) + water (x mL)), 50 °C, Ar atmosphere.

and selectivity of 2-cyclohexen-1-ol than [Fe(bpy)₃]²⁺@Y. Although the selectivity to 2-cyclohexen-1-ol on Fe-Y catalyst was similar to that on [Fe(bpy)₃]²⁺@Y catalyst, the amount of 2-cyclohexen-1-ol and H₂O₂ efficiency on the former catalyst was extremely lower than those on the latter catalyst. This result suggests that the combination of [Fe(bpy)₃]²⁺ and zeolite cage is indispensable for obtaining high 2-cyclohexen-1-ol yield with high selectivity. Thus, it was proven that [Fe(bpy)₃]²⁺@Y is a potential heterogeneous catalyst for oxidation of cyclohexene with hydrogen peroxide to 2-cyclohexen-1-ol in water. Our results are very important from the viewpoint of green chemistry because H₂O is an environment-friendly solvent.

The oxidation of cyclohexene in the presence or absence of 2,6-di-*tert*-butyl-4-methylphenol as a radical-trapping reagent gave us mechanistic information. In the presence of 2,6-di-*tert*-butyl-4-methylphenol, [Fe(bpy)₃]²⁺@Y and [Fe(bpy)₃](ClO₄)₂ exhibited no catalytic activity. This result suggests that a radical species generated from [Fe(bpy)₃]²⁺ complexes and H₂O₂ plays an important role in the oxidation mechanism. The reaction might proceed via Fenton pathway (generation of hydroxyl radicals) due to the absence of a labile site for H₂O₂ in the

complex occupied by three bipyridine ligands.^{30–33} Furthermore, the zeolite is likely to stabilize the radical species active in water, as some radical species were directly observed in zeolite by ESR.^{34–37} The reason for such a high selectivity of 2-cyclohexen-1-ol over $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y and Fe-Y may be due to coordination of hydroxy groups in generated products to Na^+ ions contained in Y-type zeolite. In this case, the oxidation of 2-cyclohexen-1-ol with hydrogen peroxide over $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y and Fe-Y to 2-cyclohexen-1-one is thought to hardly operate.

The catalytic activity of the mixture of $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ and zeolite was similar to that of the $[\text{Fe}(\text{bpy})_3](\text{ClO}_4)_2$ under homogeneous conditions. This result may support the fact that the iron complexes in $[\text{Fe}(\text{bpy})_3]^{2+}$ @Y are present inside of supercages. However, it is still not clear that the reaction proceeds inside or outside of the cage, because the size effect for a large substrate has not been examined.

In summary, we have developed mild and efficient selective hydroxylation of cyclohexene with hydrogen peroxide in water over Fe complexes encapsulated in Y-type zeolite. This discovery is expected to be a breakthrough in organic synthesis because organic solvents and/or additives are not required.

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