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Selective oxygenation of olefins with hydrogen peroxide catalyzed by iron(II) bipyridine complex included in NaY zeolite under visible light irradiation

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ABSTRACT

A novel visible light photocatalyst of iron(II) bipyridine complex encapsulated within NaY zeolite for selective oxygenation of styrene with high turnover (1800) and high benzaldehyde selectivity (86%) using hydrogen peroxide as the oxidant under ambient conditions was explored. This photocatalyst was also effective for the oxidation of other olefins, such as 4-cyanostyrene, 4-methoxystyrene, 3-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, *trans*-stilbene, *trans*-β-methylstyrene, α-methylstyrene, triphenylethylene, 1-octene, 2-octene, cyclohexene and cyclooctene, into the corresponding aldehydes, ketones or olefin oxides. The study shows that the photooxygenation of styrene occurs within the supercages of zeolite Y, the products benzaldehyde and formaldehyde escape into the solution after reaction, leading to high turnovers. Based on the experimental results, the photooxidation mechanism is also discussed.

1. Introduction

Selective oxidation of alkenes is one of the most important reactions for organic synthesis [1,2]. The stoichiometric oxidation processes, such as the epoxidation of alkenes by peracids, alkylperoxides, iodosobenzene have been widely used [3–10]. However, those processes are costly and produce large amounts of toxic byproducts. Therefore the exploration of a new oxidation process that has a minimal environment impact and low cost is necessary and remains a great challenge.

The 'green' oxidation by using environmentally friendly and cheap oxidants, such as molecular oxygen and aqueous H_2O_2, is a challenging goal of fine chemistry [11–16]. The latter has been inspired by metalloenzymes such as cytochrome P450, which utilizes a heme center for catalysis. Iron porphyrin complexes can be used as catalysts for selective oxidation of hydrocarbons. However, the susceptibility of the porphyrin to oxidative self-degradation and the usual requirement for an expensive oxidant like PhIO have limited the utilization of this approach [17]. The combination of iron complex with hydrogen peroxide is often considered to afford Habor-Weiss chemistry [18], generating hydroxyl (or alkoxyl) radicals that initiate radical chain autooxidation reactions [19,20].

In the past several years, an increasing number of studies have emerged and show that the micropores of zeolites offer an unique environment for oxidation of hydrocarbons by O_2 under visible light at much high selectivity [21–24]. Frei and coworkers succeeded in selective oxidation of hydrocarbons by O_2 in alkali and alkaline-earth exchanged zeolites under visible light irradiation [21–23]. Tung et al. investigated the microreactor-controlled product selectivity in O_2-mediated photooxidation of alkenes [25–29]. The remarkable product selectivity has been achieved in such a microreactor-controlled photoreaction. Ramamurthy et al. studied singlet oxygen mediated photooxidation of olefins within dye-exchanged X and Y zeolites [30,31]. By the utilization of zeolite supercages as 'an active reaction cavity', the activated oxygen can be directed toward a particular face of the olefins and thus a high selectivity was obtained. However, most of the reactions have been done at gas/solid interfaces or in preadsorbed states.

Herein, we report a novel iron(II) bipyridine complex catalyst encapsulated within the NaY zeolite and the photocatalytic

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oxidative performance of olefins in organic solvent using H_2O_2 with visible light irradiation under ambient temperature and pressure conditions. Styrene can be selectively photooxidized to benzaldehyde with high turnovers (1800) and high benzadehyde selectivity (86%). The photooxidation of other olefins was also examined. The study shows the photooxygenation of styrene occurs in the supercage of zeolite Y, the products benzaldehyde and formaldehyde escape out of the supercage of zeolite Y and go into the solution after reaction, which allow other styrene molecules to diffuse into the supercage of zeolite Y to further react. The reaction mechanism was investigated by ESR and XPS. The mechanistic study revealed that the active intermediates are superoxide species ($Fe^{III}BY^{\bullet}O_2{}^{\bullet-}$) and high-valent iron-oxo species ($Fe^{IV}(=O)BY$), which trigger the oxidation of the alkenes.

2. Experimental

2.1. Materials

Compounds styrene, 4-cyanostyrene, 4-methoxylstyrene, 3-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, *trans*-stilbene, *trans*-β-methylstyrene, α-methylstyrene, triphenylethylene, tetraphenylethylene, cyclohexene, 1-octene, 2-octene, benzaldehyde, styrene oxide, benzoic acid, 1-phenyl-1,2-ethanediol, 4-cyano-benzaldehyde, *p*-anisaldehyde, 3-methyl-benzaldehyde, benzophenone, acetophenone, cyclohexene oxide, 2-cyclohexen-1-one, 2-cyclohexen-1-ol, cyclooctene oxide, heptanal were purchased from Aldrich Co. Ltd. 2,2′-dipyridene and 2,2′-dipyridyl N,N′-dioxide were purchased from Acros Co. Ltd. and were used without further purification. Acetonitrile, chloroform and hydrogen peroxide were of analytical reagent grade. 5,5-Dimethyl-1-pyrroline -N-oxide (DMPO, Sigma) and 2,2,6,6-Tetramethylpiperidine (TEMP, Acros) were used as the ESR spin-trapping reagents. Ferrous perchlorate was purchased from Aldrich Co. Ltd. Deionized and doubly distilled water was used throughout this study.

2.2. Catalyst preparation

FeY was prepared by the addition of 1 g NaY to an aqueous solution of ferrous perchlorate (2 mM, 50 mL) [32]. After 24 h of gentle magnetic stirring, the ferrous ion exchanged FeY zeolite was washed, filtered and dried at room temperature under a constant N_2 flow. After ion exchange, no ferrous ion was measured in solution. This demonstrated sodium of original NaY zeolite was exchanged with iron. The exchange amount of ferrous ion on zeolite was 0.1 mmol per gram zeolite, which was calculated by measuring the concentration change of ferrous ion in the solution by a spectrophotometric method. Then 0.6 g of the 2,2-bipyridine (bpy) ligand (excessive amount of bpy to the ferrous ion) added to 1.0 g of dried FeY. The mixture was heated at 363 K for 24 h in a closed system to stimulate complex formation, then Soxhlet extracted for 24 h with dichloromethane to remove the ligands unreacted and adsorbed on the zeolite surface and dried at 323 K under nitrogen atmosphere. Thus, the iron(II) bipyridine complex/NaY catalyst (FeBY) was obtained. The catalysts with exchange amounts of 0.35, 0.18, 0.06, 0.04 mmol ferrous ions/1 g of zeolite, respectively, were also prepared. The FeBY catalyst of 0.1 mmol/g zeolite exchange amount exhibited the highest activity compared to the other four catalysts with different exchange amounts, and therefore was used for all experiments.

2.3. Photooxidation procedure

The light source was a 500 W halogen lamp (Institute of Electric Light Source, Beijing) fixed inside a cylindrical Pyrex jacket, which was surrounded by a circulating water jacket to cool the lamp. Unless otherwise noted, all the irradiation experiments were carried out in a Pyrex vessel through a potassium nitrate filter transmitting $\lambda > 330$ nm at room temperature. In a typical reaction, the substrate (4 mmol), hydrogen peroxide (30% H_2O_2 1 mL, 10 mmol), catalyst FeBY (0.5 μmol, 5 mg) and the solvent acetonitrile (5 mL) were added to the vessel (20 mL) with a sealed septum. The reaction mixture was stirred and irradiated by visible light at ambient temperature. After the reaction for the desired time, the catalyst FeBY was separated by filtration and the oxygenated products were identified, quantitatively analyzed by GC/MS and GC using toluene as an internal standard.

2.4. Instrumentation and product analysis

Gas chromatographic analysis for the reaction kinetics was performed on a HITACHI G-3900 GC spectrometer using a hydrogen flame ionization detector, equipped with an integrator processor. Nitrogen was used as the carrier gas. The inner column (length 30 m; internal diameter 0.25 mm, film thickness 0.25 μm) was packed with a SGE BP-5 5% phenyl-methyl siloxane film. The reaction products were identified by comparison of their retention times with the corresponding standard samples and conducted in a FINNIGAN TRACE DSQ GC/MS spectrometer with EI as ion source. For GC analysis of styrene oxidation reaction, the following GC conditions were used: the oven temperature was set at 100 °C, injection temperature at 200 °C, and detection temperature at 250 °C respectively. Formaldehyde was analyzed on a HP SP-502 GC spectrometer. The reaction yields were calculated on the basis of all oxidation products. The selectivity was the fraction of benzaldehyde or the aldehydes among the oxidation products formed from the photooxidation of styrene or the styrene derivatives.

Electron paramagnetic resonance (EPR) experiments were carried out on a Brucker Model ESP 300E spectrometer at ambient temperature. The irradiation source was a Quanta-Ray Nd:YAG pulsed laser system ($\lambda = 355$ nm; 10 Hz). The reaction radicals $^{\bullet}OOH/O_2{}^{\bullet-}$ and $^{\bullet}OH$ were trapped by DMPO and singlet oxygen species $^1O_2$ was trapped by TEMP. The ESR center field was set at 3486.70 G, sweep width at 100 G, microwave frequency at 9.82 GHz, modulation frequency at 100 KHz, and power at 5.05 mW. To minimize measurement errors, the same quartz capillary tube was used throughout the EPR measurements. X-ray photoelectron spectroscopy (XPS) of the samples was performed on the 220I-XL multifunctional spectrometer (VG Scientific England) using Al Kα radiation.

3. Results and discussion

3.1. Effect of light irradiation and oxidants on the oxygenation of styrene

In a typical reaction, a potassium nitrate solution was used as light filter to ensure that the styrene was not to be photo-excited by ultraviolet light. As shown in Fig. 1, potassium nitrate nearly has a 100% absorption in the region ($\lambda < 330$ nm), thus styrene does not have any absorption in the region ($\lambda > 330$ nm) using potassium nitrate as a filter. However, the catalyst FeBY and Fe(bpy-O)-Y still have absorption in the region ($\lambda > 330$ nm) using potassium nitrate as a filter. Therefore, the photooxidation of styrene was initiated by photoexcitation of catalyst FeBY, not by photoexcitation of styrene under the present conditions.

The effect of light, oxidants and different catalysts on the oxygenation of styrene was examined under different reaction conditions. Fig. 2 shows the product yield of benzaldehyde obtained after 12 h of reaction. In the dark, oxygenation of styrene catalyzed

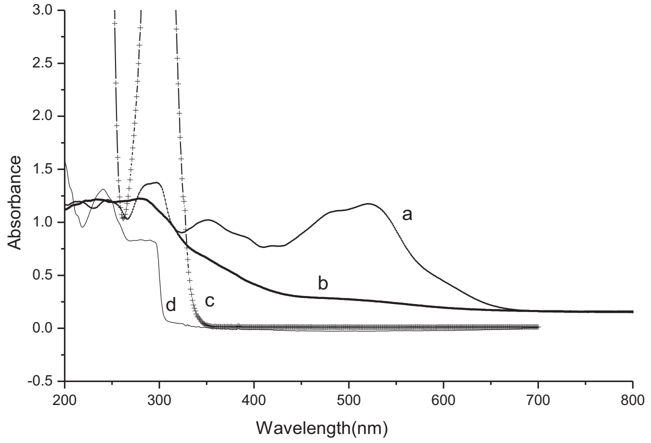


Fig. 1. UV–vis diffuse reflectance spectra of (a) FeBY and (b) Fe(bpy-O)-Y, absorption spectra of (c) 2 M KNO_3 solution and (d) 2% styrene solution in acetonitrile.

by FeBY hardly occurred in the presence of dioxygen or hydrogen peroxide (reactions A and B). Only a little amount of benzaldehyde was found in the reaction mixture, with yield of 0.25% and 1.25%, respectively. Under visible light irradiation, only benzaldehyde yield of 0.30% and 1.13% was obtained for dioxygen and hydrogen peroxide as oxidants (C and D), respectively, in the absence of catalyst FeBY. Under visible light irradiation, selectively catalytic oxygenation of styrene to benzaldehyde by FeBY with a yield of 23% and selectivity of 86% was achieved for hydrogen peroxide as the oxidant (F). Besides the major product of benzaldehyde, a small amount of 1-phenyl-1,2-ethanediol and benzoic acid were also formed.

Under these conditions (F), a high turnover of 1800 (moles styrene consumed/moles Fe in FeBY) was obtained. However, photooxygenation of styrene with dioxygen hardly occurred in the presence of FeBY under otherwise identical conditions, with less than 1% benzaldehyde yield (E). Therefore visible light irradiation, the catalyst FeBY and hydrogen peroxide are indispensable for the photooxygenation of styrene in this system. In the presence of NaY zeolite (G) or bipyridine/NaY zeolite (H), photooxygenation of styrene with hydrogen peroxide as oxidants was only achieved with lower benzaldehyde yield of 6.21% and 4.3%, respectively, under visible light irradiation. This indicates that synergistic interaction of NaY zeolite and iron (II) bipyridine complex promotes the photooxygenation of styrene with hydrogen peroxide under visible irradiation.

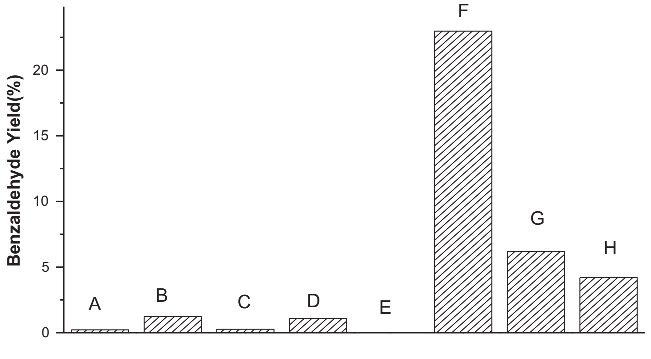


Fig. 2. The product yield of benzaldehyde obtained after 12 h of reaction under the following conditions: (A) in the dark in the presence of FeBY and O_2; (B) in the dark in the presence of FeBY and H_2O_2; (C) O_2 as oxidant in the absence of FeBY under visible light irradiation; (D) H_2O_2 as oxidant in the absence of FeBY under visible light irradiation; (E) in the presence of FeBY and O_2 under visible light irradiation; (F) in the presence of FeBY and H_2O_2 under visible light irradiation; (G) in the presence of NaY and H_2O_2 under visible light irradiation; (H) in the presence of NaY, bipyridine and H_2O_2 under visible light irradiation. Reaction conditions: styrene 4 mmol, H_2O_2 10 mmol, FeBY 5 mg (0.5 μmol), NaY 15 mg, acetonitrile 5 mL.

3.2. Photooxygenation of other olefins with hydrogen peroxide

The photooxygenation of other terminal and internal olefins with hydrogen peroxide catalyzed by FeBY was also investigated, in which 4-cyanostyrene, 4-methoxylstyrene, 3-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, *trans*-stilbene, *trans*-β-methylstyrene, α-methylstyrene, triphenylethylene, tetraphenylethylene, cyclohexene, cyclooctene, 1-octene, 2-octene were selected as model substrates (Table 1). The experimental results indicated that aromatic terminal and internal olefins such as 4-cyanostyrene, 4-methoxylstyrene, 3-methylstyrene, 1,1-diphenylethylene, *cis*-stilbene, *trans*-stilbene, *trans*-β-methylstyrene, α-methylstyrene, triphenylethylene could be selectively oxidized to corresponding carbonyl compounds with high selectivity and high turnovers catalyzed by FeBY under visible irradiation. Interestingly, alphatic terminal alkene 1-octene was also partly photooxidized to heptanal with C═C double bond oxidative cleavage besides 1-octene oxide. However, alphatic internal alkene such as 2-octene was only photooxygenated to 2-octene oxide without C═C double bond oxidative cleavage under the present conditions. In addition, cyclooctene was oxidized to cyclooctene oxide, while cyclohexene was photooxidized to cyclohexene oxide, 2-cyclohexen-1-one and 1,2-dihydroxylcyclohexane. This indicates that the aromatic alkenes can be selectively photooxidized to the corresponding carbonyl compounds with C═C double bond oxidative cleavage catalyzed by FeBY in the presence of hydrogen peroxide, while the alphatic alkenes are photooxidized to alkene oxides besides carbonyl compounds.

3.3. Recycling experiments

Recycling tests with repeated use of FeBY in three consecutive reactions were carried out. The catalyst was separated from the reaction mixture by filtration after 8 h reaction. It was then washed with acetonitrile, calcined at 100 °C for 4 h, and subjected to the next catalytic run under the same reaction conditions. In three consecutive photooxidation of styrene (styrene 4 mmol, FeBY 0.5 μmol/5 mL acetonitrile), the yield of benzaldehyde was 19.2%, 20.1%, 19.6%, respectively. No obvious catalytic activity loss of FeBY indicates no blocking of the access channels to the active site and no metal complex leaching. Meanwhile, neither metal iron Fe^{2+}/Fe^{3+} nor bipyridine/its degraded intermediates was detected in the reaction mixture using the spectrophotometric method [33]. This indicates that the catalyst FeBY has good stability in recycling experiments.

3.4. Effect of zeolite supercage

The zeolite used in all of the experiments reported here is the honeycomblike Y zeolite characterized by four 7.4 Å windows tetrahedrally arranged around a 13 Å diameter supercage. In order to examine the effect of zeolite supercage, catalyst FeBY was heated in a tube oven at 100 °C under aerated conditions for 12 h. The sample was then transferred to a desiccator and allowed to cool to room temperature. To a acetonitrile solution (5 mL) of styrene (100 μL), 50 mg of pretreated FeBY was added and stirred for 5 h. Subsequently, styrene-preadsorbed FeBY was separated by filtration. The styrene loading amount was calculated by measuring the styrene amount in the solution acquired by digestion of styrene loaded FeBY with 10% HCl and then extraction with THF

Table 1
Visible light photooxidation of olefins with hydrogen peroxide catalyzed by FeBY.

substrate	Reaction time (h)	Main products	Yield (%)	Selectivity (%)	TON
Styrene	9	benzaldehyde	23.2	86	1856
4-Methoxylstyrene	9	*p*-anisaldehyde	19.7	93	1376
4-Cyano-styrene	9	4-cyano-benzaldehyde	10.6	90	848
3-Methylstyrene	8	3-methyl-benzaldehyde	12.9	90	1032
Trans-β-methylstyrene	8	benzaldehyde	34.5	92	2760
α-Methylstyrene	8	acetophenone	34.9	90	2792
1,1-Diphenylethylene	8	benzophenone	18.6	90	1488
Cis-stilbene	8	benzaldehyde	29.2	93	1168
Trans-stilbene	8	benzaldehyde	45.1	95	1263
Triphenylethylene	8	benzophenone	13.1	47	71
		benzaldehyde	10.6	46	57
Tetraphenylethylene	8	—	no reaction	—	
1-Octene		1-octene oxide	6.2	67	496
		heptanal	3.0	33	240
2-Octene	9	2-octene oxide	8.2	97	656
Cyclohexene	8	cyclohexene oxide	5.3	30	424
		2-cyclohexen-1-one	5.4	30	432
		1,2-dihydroxyl-cyclohexane	7.2	40	576
Cyclooctene	8	Cyclooctene oxide	29.1	99	2328

Reaction conditions: acetonitrile 5 mL, H_2O_2 30% 10 mmol, olefin 4 mmol except *trans*-stilbene (2.8 mmol) and triphenylethylene (0.27 mmol), catalyst FeBY 5 mg (0.5 μmol). TON (turnover number): moles styrene consumed/moles Fe in FeBY.

or CH_2Cl_2. The styrene loading amount was only 0.02 molecules per supercage. This maybe due to the presence of iron bipyridine complex in the zeolite Y (loading amount of iron bipyridine is 0.19 molecules per supercage). Fresh acetonitrile (5 mL) and hydrogen peroxide were added to the styrene- preadsorbed FeBY and then subjected to irradiation through a potassium nitrate filter for desired time. After stirring for 30 min before photoreaction, no styrene was detected in the acetonitrile solution. This indicates that the styrene molecules still existed in the supercage of zeolite before photoreaction. After the photoreaction, the FeBY was separated by filtration from the acetonitrile solution. The FeBY catalyst was digested with 10% HCl and then was extracted with THF or CH_2Cl_2. Both the extracted solution and the filtrate acetonitrile solution were subjected to GC analysis. GC analysis indicated that neither styrene nor its products were detected in the extracted solution, however, in the filtrate acetonitrile solution, the product benzaldehyde was detected with 100% selectivity and 100% styrene conversion. The results demonstrate that the photooxygenation of styrene with hydrogen peroxide catalyzed by FeBY occurs in the supercage of zeolite Y. After the reaction, the product benzaldehyde freely diffuses out of the supercage of zeolite and into the bulk solution. This ensures that other styrene molecules can diffuse into the supercage of zeolite Y and react with hydrogen peroxide, followed by benzaldehyde escaping into the solution. In place of acetonitrile, the same phenomenon occurred in hexane solution.

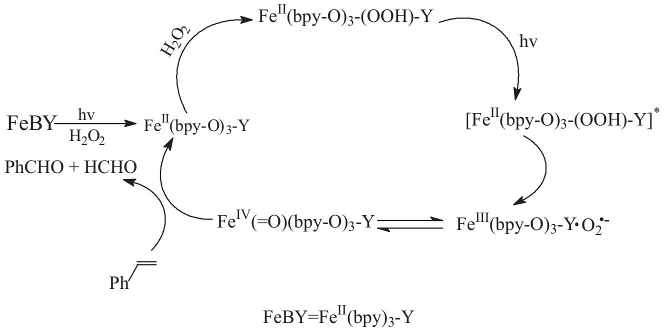
The oxygenation of triphenylethylene and tetraphenylethylene was examined in the presence of FeBY and hydrogen peroxide under visible light irradiation (see Table 1). Experimental results revealed that triphenylethylene was oxidized to benzaldehyde and benzophenone with high selectivity, however, oxygenation of tetraphenylethylene hardly occurred. This implies that triphenylethylene molecule can diffuse into the supercage of zeolite Y through the phenyl moiety. However, tetraphenylethylene molecule can not diffuse into the supercage of zeolite Y through the zeolite channel since the distance between the two phenyl moiety is larger than 7.4 angstrom. This further demonstrates that the photooxygenation of olefins catalyzed by FeBY occurs in the supercage of zeolite Y, the oxygenated products escape into the solution after the reaction, then the other substrate molecules can diffuse into the supercage of zeolite Y to react further.

3.5. Reaction mechanism of photooxidation

On the basis of the above results and the experiments described below, a possible reaction mechanism for the photooxygenation of styrene catalyzed by FeBY is summarized in Scheme 1.

It was found that, at the beginning of reaction, the catalyst FeBY is oxidized to Fe(bpy-O)-Y by hydrogen peroxide under visible light irradiation, as evidenced by XPS spectra (Fig. 3). In the XPS spectra (Fig. 3), the XPS spectra of Fe(bpy-O)-Y catalyst (prepared with 2,2′-dipyridyl-N,N′-dioxide) and the catalyst of oxidized FeBY by hydrogen peroxide under visible irradiation are virtually identical, which are different from the spectra of original FeBY catalyst. The Fe(bpy-O)-Y and oxidized FeBY catalyst all show the presence of two nitrogen bands (N1s; binding energy (BE) 399.4 ev, 402.4 ev), however, the FeBY catalyst only show the presence of one nitrogen bands (N1s; binding energy (BE) 399.5 ev). In the XPS spectra, one peak at 399.4 eV was assigned to sp^2 bonding, and another peak at 402.4 eV was assigned to N—O bonding, in accord with the literature [34,35]. In order to confirm this, the Fe(bpy-O)-Y was also prepared using bpy-O as the ligand similar to preparation of FeBY and photooxidation of styrene catalyzed by Fe(bpy-O)-Y was performed in the presence of hydrogen peroxide. A similar benzaldehyde yield of 19.6% and selectivity of 86% were achieved.

The active oxygen radical intermediates involved in photooxidation of styrene were detected using EPR technique. Upon light



Scheme 1. Proposed reaction mechanism of photooxidation of styrene catalyzed by FeBY with hydrogen peroxide under visible light irradiation.

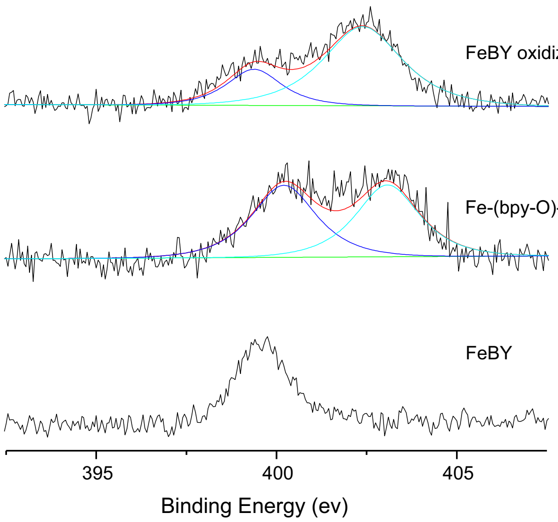


Fig. 3. X-ray photoelectron spectrum of several catalysts. Lower: FeBY; middle: synthetic Fe(bpy-O)-Y (preparation method is the same as that of FeBY), upper: sample after FeBY was photooxidized with hydrogen peroxide under visible light irradiation.

irradiation ($\lambda = 355$ nm) in the presence of DMPO as a radical trapping agent, the characteristic six peaks in the ESR spectrum of DMPO-$^{\bullet}OOH/O_2^{\bullet-}$ adducts were observed in the reaction system, and the intensity increased slightly with irradiation time as shown in Fig. 4. However, no $^{\bullet}OH$ radicals and singlet oxygen species were observed in the photoreaction system. In the control experiments, no signals with a significant intensity were observed in the FeBY/H_2O_2 system in the dark. In another experiment, it was found that the addition of SOD [41] (superoxide dismutase) to the photooxidation system significantly suppressed the photooxidation of styrene. SOD [41] is a known efficient quencher of radicals $^{\bullet}OOH/O_2^{\bullet-}$, so this could indicate that the $^{\bullet}OOH/O_2^{\bullet-}$ radicals diffuse out of the zeolite. However, it could also mean that SOD mechanically blocks the zeolite pores. Additionally, addition of benzene or acetone, known scavengers of $^{\bullet}OH$ radicals, into the reaction system did not cause any apparent suppression in the photooxygenation of styrene. This indicates that the $^{\bullet}OH$ radicals and singlet oxygen are not the main active oxygen species involved in the photooxygenation of styrene catalyzed by FeBY. The $^{\bullet}OOH/O_2^{\bullet-}$ radicals or the subsequent converted form (high valent iron-oxo species $Fe^{IV}{=}O$) [34–38] formed by activation of hydrogen peroxide should be the main oxygen species for this photoreaction.

As illustrated in Scheme 1, the Fe(II)(bpy-O)-Y complex in combination with H_2O_2 gives the nucleophilic adduct Fe(II)(bpy-O)-(OOH)-Y. Under visible irradiation, this species further converts into Fe(III)(bpy-O)-Y$^{\bullet}O_2^{\bullet-}$, as evidenced by EPR measurements, or the subsequent converted form $Fe^{IV}{=}O$ [36–40], which reacts with styrene to form benzaldehyde and formadehyde.

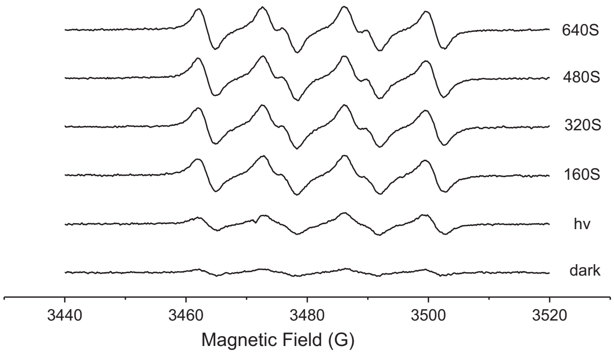


Fig. 4. The EPR signals of the DMPO- $^{\bullet}OOH/O_2^{\bullet}$ adducts in styrene/H_2O_2/Fe(bpy-O)-Y system in the dark and under UV irradiation (pulsed laser system: $\lambda = 355$ nm; 10 Hz). Styrene: 0.2 M, DMPO: 0.04 M, Fe(bpy-O)-Y: 0.1 mM, H_2O_2: 0.2 mM, solvent: acetonitrile.

4. Conclusions

A novel visible photocatalyst for selective oxygenation of styrene with high turnover and good chemoselectivity using hydrogen peroxide as oxidant is reported. The study shows that the photooxygenation of styrene occurs in the supercage of zeolite Y. The products benzaldehyde and formaldehyde easily escape into the solution after reaction, which allow other styrene molecules to further diffuse into the supercage of zeolite Y to react, leading to very high turnover number and good chemoselectivity. The main active oxygen species involved in this photoreaction is superoxide anion radicals or the subsequent converted form (high valence iron-oxo species $Fe^{IV}{=}O$). Using this photocatalyst, several other olefins were also photooxygenated to the corresponding carbonyl compounds or olefin oxides.

Acknowledgments

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