

A highly selective photooxidation approach using O₂ in water catalyzed by iron(II) bipyridine complex supported on NaY zeolite

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A new photocatalytic system involving iron(II) bipyridine supported on NaY zeolite (FeBY) shows excellent reactivity and selectivity in the oxidation of organic compounds. This approach allows highly controlled oxidation reaction to occur but avoids undesirable mineralization into CO₂ and H₂O.

'Green' oxidation, using hydrogen peroxide or ideally molecular oxygen (or air) as the oxidant and water as the solvent, is the most economically attractive and environmentally friendly oxidation technology used in selective organic synthesis and treatment of organic pollutants. In the past several years, it has been found that the micropores of zeolites offer an environment for oxidation of hydrocarbons by O₂ at very high selectivity.^{1–4} Recently, Frei *et al.* reported a selective gas-phase photooxidation of hydrocarbons by O₂ in alkali and alkaline-earth exchanged zeolites under visible light irradiation.⁵ Ramamurthy and coworkers also demonstrated remarkable selectivity in the formation of hydroperoxides from alkenic systems through a singlet oxygen mechanism by using dye-exchanged zeolites in hexane solvent.⁶ Recently, we found that iron(II) bipyridine supported on a resin (FeBR) can efficiently activate molecular oxygen to degrade organic pollutants (rhodamine B (RhB), malachite green (MG) and *N,N*-dimethylaniline (DMA)) in water under visible light irradiation, and the total organic carbon (TOC) removal yields were 60%, 58% and 75%, respectively.⁷ It should be noted that a high degree of mineralization is not necessarily desirable in photochemical reactions. In organic synthesis, for example, it is much more important to selectively oxidize the reactants than to convert them all the way to CO₂ and H₂O. In this work, we combined the photocatalytic oxidation power of a supported iron(II) bipyridine with the high selectivity of a zeolite network. This approach was applied successfully to selectively oxidize MG under visible light irradiation. Interestingly, undesirable mineralization could be avoided as indicated by the nearly zero% TOC removal.

The iron(II) bipyridine complex was supported on a NaY (Si/Al = 5) zeolite (FeBY) by a stepwise method.⁸ The UV–Vis diffuse reflectance spectra show that the FeBY displays a broad adsorption band in the region of 240–700 nm with a maximum absorption at 522 nm, and neither FeY nor NaY has absorption in the visible region. We also employed X-ray photoelectron spectroscopy to characterize the catalyst. The result shows that the signals of iron of the catalyst before and after photoreaction are virtually identical, and they are attributed to Fe^{II} species (2p_{3/2}; binding energy 708.85 eV).

Malachite green (MG), the structure is shown in Fig. 1) was used as a model compound. The photooxidation process of MG has been examined in detail in the other systems. It was found that MG can be readily mineralized into CO₂ to a great extent in all the systems we employed before.^{7,9} The selective photooxidation of MG catalyzed by FeBY was examined in the present work under visible light irradiation.¹⁰ Before the irradiation, a time period of an hour was allowed to ensure the establishment of adsorption/desorption equilibrium between FeBY and MG. As the reaction proceeded, the absorption peak intensity of MG decreased and new absorption peaks at 365 nm

and 251 nm emerged (Fig. 1), and they are attributed to the absorption of aminobenzophenone as evidence by the authentic samples and GC–MS results (see below). Fig. 1 insert shows the variations in the concentration of MG under different conditions. No significant reaction of MG was observed either in the dark in the presence of FeBY (curve a), with bubbling helium gas under visible light (curve b), or in the blank experiment under visible irradiation. However, MG was discoloured rapidly in the presence of FeBY in an aerobic solution under visible irradiation (curve c). Evidently, both visible light irradiation and O₂ are indispensable for the oxidation of MG in this system. 90% of MG was transformed catalytically by FeBY after 240 min of irradiation. The colour of the catalyst turned from red to blue when MG was adsorbed, and then back to red after irradiation for 300 min. In the control experiments, less than 15% of MG was degraded in the presence of zeolite NaY or NaY loaded by iron(II) under the visible light irradiation for 5 hours, and it may be attributed to the Frei mechanism.⁵ The consecutive oxidation of MG (4 cycles) in the same solution showed that the catalyst had good stability. During the photoreaction, none of Fe(bpy)₃²⁺, free Fe²⁺/Fe³⁺ ions, bipyridine or its degraded species were detected in the solution. Zero-order kinetics were obtained ($k_{vis} = 5.8 \times 10^{-8} \text{ mol L}^{-1} \text{ min}^{-1}$), and the catalyst : substrate molar ratio can reach to 1 : 20. This indicates that FeBY is an excellent photocatalyst in the oxidation of MG in water by activating O₂ under visible light irradiation.

The oxidation products of MG in the cycle reaction were identified by gas chromatography–mass spectrometry (GC–MS). The products are listed in Table 1 together with their retention times and peak areas in the chromatogram. Because of the influence of the dimethylamino groups, MG tends to cleave at the bond between the central carbon atom and dimethylaminophenyl moiety. This is consistent with the GC–MS results that the most abundant products are 4-dimethylaminobenzophenone (E) and 4-methylaminobenzophenone (F). With the exception

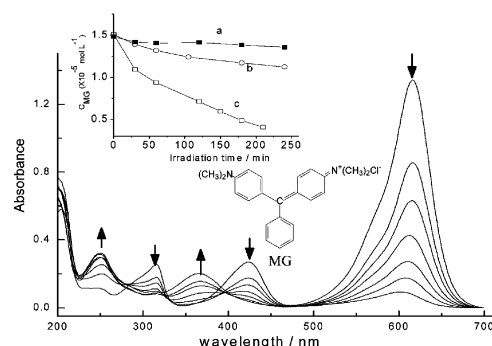


Fig. 1 The UV–vis absorption spectral changes of the MG solution as a function of irradiation time in a FeBY system under visible light irradiation. The inset shows the variations in concentration of MG under different conditions: (a) in the presence of FeBY in the dark, (b) in the presence of FeBY bubbling with helium under visible light irradiation, (c) in the presence of FeBY under visible light irradiation. FeBY (0.1 g l⁻¹), MG (2 × 10⁻⁵ M); pH = 4.6.

Table 1 GC-MS data and identified molecular structures of products formed in the photooxidation of MG

Peak	Products	Retention time/min	Peak area (%)
A	Methyl benzoate	7.05	1.0
B	<i>N,N</i> -Dimethylaniline	12.37	0.4
C	Hydroquinone	13.29	6.4
D	4-Aminobenzophenone	21.72	0.3
E	(4-Dimethylamino)benzophenone	22.15	51.7
F	(4-Methylamino)benzophenone	22.50	37.5
G	(4-Dimethylamino-4'-methylamino)benzophenone	23.25	0.9
H	Malachite green	27.71	1.2

of *N*-demethylation, these products were formed from the oxidation of the central carbon atom of MG. TOC measurements show almost no change in the total organic content before and after photooxidation. This suggests that the process is a selective oxidation rather than a mineralization.

The effect of subsequent UV irradiation after the complete bleaching of MG was also studied. Neither further oxidation nor mineralization was observed when the reaction system was irradiated by a 100 W Hg lamp. Moreover, the same reaction products were obtained when we employed the UV source at the initial stage of the reaction. These observations illustrate that the excitation wavelength does not affect the selectivity of the FeBY photocatalytic system. This is different from Frei's system¹¹ in which the reaction selectivity is dependent on the wavelength of irradiation. In our system the FeBY but not the substrate-O₂ complex (as in Frei's system) is excited.

We also examined the photooxidation of acridine orange, methylene blue and bright green in aqueous solutions in the presence of FeBY under visible light irradiation. It was found that they could all be easily bleached in a short time without any changes in TOC values. Additionally, in the photooxidation of styrene, benzaldehyde was obtained after irradiation for 2 hours. This provides sufficient evidence that the FeBY system possesses good photocatalytic reactivity by oxidising the organics through the activation of molecular O₂ under visible light irradiation.

EPR was employed to provide useful information on the active radical intermediates.¹² Upon visible light irradiation ($\lambda > 420$ nm), the six peaks of DMPO-OOH/O₂^{•-} (DMPO, 5,5-dimethylpyrroline *N*-oxide) adducts were observed in the MG/FeBY system, and the intensity increased slightly with the irradiation time (Fig. 2). These results confirmed that •OOH/O₂^{•-} radicals are generated from the activation of molecular oxygen in the photocatalytic process. In the control experiments no signals with a significant intensity were observed in the MG/FeBY system in the dark, or in the MG/NaY system under visible light irradiation. SOD, an efficient scavenger for O₂^{•-}, was added into the FeBY/MG system, and it was found that addition of SOD effectively suppressed the photooxidation of

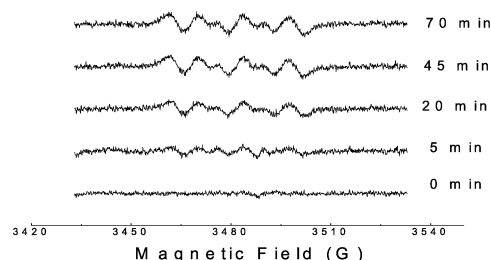


Fig. 2 EPR signals of the DMPO-OOH/O₂^{•-} adducts as a function of visible illumination time. DMPO (0.15 M), pH = 4.6.

MG. We also employed NaN₃ as the singlet oxygen quencher,¹³ and it had little effect on the photoreaction. In EPR experiments, no •OH radicals were detected under the experimental conditions, and it was also found that addition of isopropanol, a known scavenger of •OH radicals, into the reaction system did not cause any apparent changes in the photooxidation. This indicates that singlet oxygen and the •OH radicals are not the main active oxygen species involved in the photoreaction catalyzed by FeBY. The O₂^{•-} radicals or the subsequent converted form (high valent iron-oxo species Fe^{IV}=O)^{14,15} formed by activation of molecular O₂ must be the main active oxygen species for this photoreaction. The special structure of the zeolite NaY provides a unique microenvironment for the active sites of Fe(bpy)₃²⁺ and leads to the high photoreaction selectivity. The high-valent iron-oxo species (Fe^{IV}=O) as the active intermediate are also reported by Collins' group based on another N-donor ligand system.¹⁶ According to their notion, iron-oxo reactive intermediates are still very reactive but more selective than the reactive intermediates of Fenton's systems. In the FeBY system, we proposed that the active intermediates were superoxide species (L₃Fe^{III}O^{•-}) and high-valent iron-oxo species (L₃Fe^{IV}=O), which eventually triggers the oxidation of the target organic compound. Further study is needed for the detailed reaction mechanism.

Notes and references

- 1 J. C. Scaiano and Hermenegildo Garcia, *Acc. Chem. Res.*, 1999, **32**, 783.
- 2 A. Maldotti, A. Molinari and R. Amadelli, *Chem. Rev.*, 2002, **102**, 3811.
- 3 R. F. Parton, Ivo F. J. Vankelecom, Mark J. A. Casselman, C. P. Bezoukanova, J. B. Uytterhoeven and P. A. Jacobs, *Nature*, 1994, **370**, 541.
- 4 P-P. Knops-Gerrits, D. De Vos, F. Thibault-Starzyk and P. A. Jacobs, *Nature*, 1994, **369**, 543.
- 5 F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1993, **115**, 7501; F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1994, **116**, 1812; H. Sun, F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1994, **115**, 7951; F. Blatter, H. Sun, Vasenkov and H. Frei, *Catal. Today*, 1998, **41**, 297.
- 6 X. Li and V. Ramamurthy, *J. Am. Chem. Soc.*, 1996, **118**, 10666; R. J. Robbins and V. Ramamurthy, *Chem. Commun.*, 1997, 1071.
- 7 W. Ma, J. Li, X. Tao, J. He, Y. Xu, J. C. Yu and J. Zhao, *Angew. Chem., Int. Ed.*, 2003, **42**, 1299.
- 8 FeY was prepared by ion exchanged of NaY (1 g) with a 2 mM aqueous solution of FeCl₂ (50 ml). The FeY zeolite was then washed, filtered and dried at room temperature under a N₂ flow. 0.6 g of the bpy ligand was 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, and Soxhlet-extracted for 24 h with CH₂Cl₂ to remove the unreacted ligand and then dried at 323 K under nitrogen atmosphere.
- 9 F. Chen, W. Ma, J. He and J. Zhao, *J. Phys. Chem. A*, 2002, **106**, 9485; Y. Xie, F. Chen, J. He, J. Zhao and W. Ma, *J. Photochem. Photobiol. A: Chem.*, 2000, **136**, 235; F. Chen, J. He, J. Zhao and J. C. Yu, *New J. Chem.*, 2002, **36**, 336.
- 10 All the irradiation experiments were carried out in a Pyrex vessel A 500 W halogen lamp as a visible light source was positioned within a cylindrical Pyrex Vessel. A Pyrex jacket with water circulation was used to cool the lamp. A light filter to cut completely light below 420 nm was placed outside the Pyrex jacket to guarantee irradiation with visible light.
- 11 F. Blatter, H. Sun and H. Frei, *Catal. Lett.*, 1995, **35**, 1; H. Frei, F. Blatter and H. Sun, *CHEMTECH*, 1996, 24.
- 12 J. Zhao, T. Wu, K. Wu, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, 1998, **32**, 2394.
- 13 In the experiments of additives, 10, 20, 50, and 80 equivalents of isopropanol and sodium azide *versus* MG (2×10^{-5} M) were employed.
- 14 L. Weber, R. Hommel, J. Behling, G. Haufe and H. Hennig, *J. Am. Chem. Soc.*, 1994, **116**, 2400.
- 15 R. Richman and M. Peterson, *J. Am. Chem. Soc.*, 1982, **104**, 5795.
- 16 T. Collins, *Acc. Chem. Res.*, 2002, **35**, 782.