Science in China Series B: Chemistry

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Zeolite NaY-mediated oxidation of dyes with H_2O_2: unique heterogeneous non-transition metal center cleavage of H_2O_2 under visible light irradiation

LIU LiLi[1], MA WanHong[1†], SONG WenJing[1], CHEN ChunCheng[1], LIN Jun[2], ZHAO JinCai[1†], QIAN XinHua[3] & ZHANG ShiBo[3]

[1] Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China;
[2] Department of Chemistry, Renmin University of China, Beijing 100872, China;
[3] Fushun Petrochemical Company, PetroChina Company Limited, Fushun 113008, China

This study investigated the visible-light catalysis mediated by zeolite NaY on the oxidation of dyes with H_2O_2. The results demonstrated that zeolite NaY acts as a sink for the electron from the photo-excited dye in the heterogeneous catalysis. Furthermore, the electron can effectively activate H_2O_2 to produce $^{\bullet}OH$ radical that is a powerful oxidant for the oxidation of dye at room temperature. The effects of the framework topology, Si/Al ratio, and exchangeable cation of the zeolite on the oxidation of various dyes were also shown.

photooxidation, zeolite NaY, dye, hydrogen peroxide, visible light

Unlike the Lewis acid catalyzed reactions inside zeolites under high temperature (>400℃), inserted transition metal Fe, Mn, Co, or Ni complex into zeolites, via reversible redox transformation of metal center, can selectively oxidize hydrocarbon at room temperature[1−4]. Organic oxidants, such as iodosobenzene, *t*-butylhydroperoxide or *m*-chloroperoxybenzoic acid, and apolar organic solvent are used in most of these systems[2,5−7]. Currently, to meet the demand of green chemistry, it is favorable to use H_2O_2 as oxidant and H_2O as solvent for the oxidation reactions because H_2O_2 does not produce any side-product besides water. Many successful cases for activation of H_2O_2 by transition metal complex in zeolites are well demonstrated in the heterogeneous catalysis. However, for a practical application, there is a serious drawback that the transition metal complex may not be stable enough against $^{\bullet}OH$ radicals produced in the system. In present work, it was found that zeolite NaY is active for catalytic oxidation of selective organic dyes with H_2O_2 under visible light irradiation. It was evidenced that the electron transfer from the excited dyes inside the supercages of zeolite NaY can efficiently cause the decomposition of H_2O_2 to produce $^{\bullet}OH$ radicals. The formed $^{\bullet}OH$ radicals are responsible for the oxidation of the dyes. This work provides a novel version of zeolite-mediated oxidation for green chemistry using H_2O_2 as oxidant, water as solvent, and solar light as clean energy. More importantly, it demonstrates the possibility of electron transfer between an organic target and H_2O_2 via zeolite under visible light irradiation.

1 Materials and methods

1.1 Chemicals

Malachite green, Fuchsin basic, Methyl violet, Thionine, Rhodamine 6G, Orange Ⅱ, benzyltrimethylammonium chloride, and hydrogen peroxide were of laboratory reagent grade quality and were used without further puri-

Received November 20, 2006; accepted August 20, 2007
doi: 10.1007/s11426-007-0138-1
†Corresponding author (email: jczhao@iccas.ac.cn, whm@iccas.ac.cn)
Supported by the 973 Program of China (Grant No. 2003CB415006), the National Natural Science Foundation of China (Grant Nos. 20520120221, 20537010, 50436040, 20371048, 20407016) and the Chinese Academy of Sciences

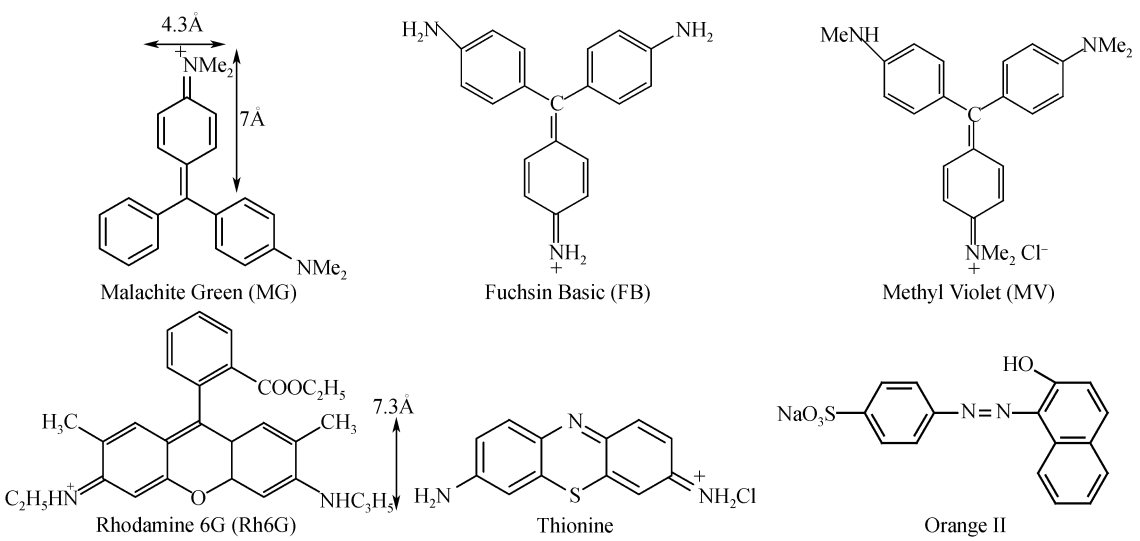
fication. The spin trap 5, 5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from the Sigma Chemical Co. Deionized water was used throughout this study. The structures of all dyes used in this work are shown in Scheme 1.

1.2 Zeolite

NaY (Si/Al=2.4 and 3.7), ZSM-5 zeolite, and MCM-41 were commercial samples. NaY possesses supercages of approximately 13 Å in diameter, connected with each other via 12-membered ring openings of 7-8 Å dimension. ZSM-5 is a bidirectional zeolite with the two effective window sizes of 5.3×5.6 Å and 5.1×5.5 Å. Compared to zeolite Y, ZSM-5 has a smaller pore size so that most of the dye molecules cannot plunge into its channels. MCM-41 is a mesoporous silica zeolite (~2 nm) and permits free migration of dye molecules in the host frameworks. HY was prepared by exchanging Na^+ with NH_4^+ three times followed by calcinations as reported in the literature[8]. FeY zeolite was obtained by liquid-state ion exchanged method with 50 mL of 1×10^{-3} mol·L^{-1} $Fe(ClO_4)_3$ solution and 1 g NaY. FeY, HY, and NaY possess almost the same supercages and different countercations.

1.3 Experimental

A 500 W halogen lamp (Institute of Electric Light Source, Beijing) was positioned inside the cylindrical Pyrex glass reactor that was surrounded by a circulating water jacket (Pyrex) to cool the lamp. An appropriate cutoff filter was placed outside the Pyrex jacket to ensure complete removal of radiation below 450 nm and to ensure that the irradiation of the dispersion was achieved only by visible light wavelengths. Aqueous suspensions of MG (usually 50 mL, 2×10^{-5} mol·L^{-1}), aqueous H_2O_2 (1×10^{-4} mol·L^{-1}) and 1.5 mg of catalyst powders (zeolite) were placed in the Pyrex vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under ambient air-equilibrated conditions. At given irradiation time intervals, 3 mL samples were analyzed by recording variations at the wavelength of maximal adsorption (for MG λ_{max} = 616 nm) in the UV-vis spectra of MG using a Hitachi U-3010 spectrometer. The experiments for the oxidation of other dyes were conducted in the same manner as above. The photooxidation products of MG were identified using ESI-MS (APEX Ⅱ model FT-TCR mass spectrograph). ESR spectra were obtained using a Bruker model ESP 500 E electron paramagnetic resonance spectrometer equipped with a QuantaRay Nd:YAG laser system as the irradiation light source (λ = 532 nm), and the same quartz capillary tube was used to minimize the errors during the measurements. Hydrogen peroxide was analyzed photometrically by the POD (horseradish peroxidase)-catalyzed oxidation product of DPD (*N*, *N*-diethyl-*p*-phenylenediamine) at λ = 551 nm (ε = 21000 L·mol^{-1} cm^{-1}).



Scheme 1 Structures of various dyes.

2 Results and discussion

Malachite Green (MG) was used as a model molecule to examine the catalytic activity of NaY under visible irradiation ($\lambda > 450$ nm) in water. Figure 1(a) shows that MG could be oxidized effectively by H_2O_2 in the presence of NaY under visible light irradiation, while in the dark the oxidation of substrate was negligible. After irradiation for 12 h, both the bulk solution and the NaY zeolite particles discolored completely. Moreover, without the zeolite, little of MG could be oxidized with H_2O_2 under visible light, indicating inefficiency of the homogenous photoreaction of H_2O_2 with the substrate.

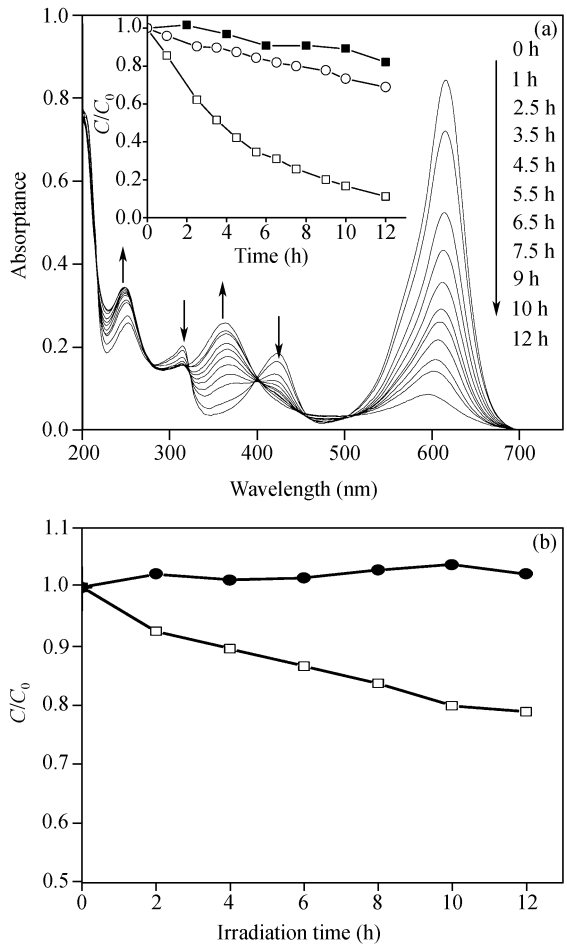
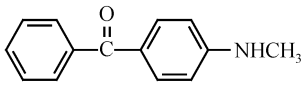
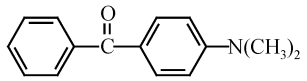
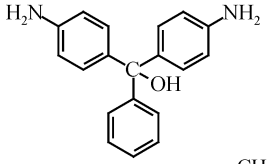
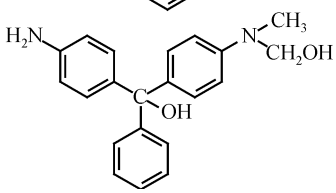


Figure 1 (a) Changes of the absorption spectra and photooxidation of MG under different conditions (inset). □, MG/H_2O_2/NaY with visible light; ■, MG/H_2O_2/NaY in the dark;○, MG/H_2O_2 with visible light. (b) Decomposition of H_2O_2 corresponding to the MG oxidation with visible light: □, MG/H_2O_2/NaY; ●, H_2O_2/NaY. MG = 2×10^{-5} mol·L^{-1}; NaY = 1.5 mg/50 mL; $H_2O_2 = 2\times10^{-4}$ mol·L^{-1}, pH=7.

More interesting behavior is that the decomposition of H_2O_2 did not occur under visible light irradiation in the presence of NaY alone or after MG turned completely colorless (Figure 1(b)). However, in the presence of both substrate MG and NaY, the decomposition of H_2O_2 was observed concomitantly with the oxidation of the substrate under visible light irradiation. From ESI-MS results (Table 1), the main oxidation products were aminobenzophenone compounds, such as 4-methylaminobenzophenone and 4-dimethylaminobenzophenone. In addition, TON[9] was calculated to be about 2.47 (molecules/supercage). The result indicates that the dye is out of the supercage of NaY after oxidation, leaving the space for a new substrate to refill in.

Table 1 Oxidation products identified by positive ion mode (M+H) electrospray mass spectra (ESI-MS) in the photooxidation of MG in the presence of NaY/H_2O_2 under visible light irradiation

Peak	*m*/*z*	Product
A	60.1	$HCONHCH_3$
B	212.1	
C	226.2	
D	248.2	unidentified
E	264.1	unidentified
F	291.1	
G	335.2	

The framework topology and chemical composition (Si/Al ratio and exchangeable cation) of zeolites were found to significantly influence the photooxidation activity. Much less MG was oxidized in ZSM-5 case than in NaY case because its smaller pore size prevents MG (diameter of one arm is about 4.3 Å and length is about 7 Å) from freely plunging into the active centers of ZSM-5 (Figure 2). The photooxidation of the larger molecule rhodamine 6G (Rh6G) further proved the effect of cavities and channels. Rh6G molecular diameter (~7.3 Å) is between the pore sizes of ZSM5 and NaY. Experiment showed that Rh6G photooxidation occurred only in NaY case (Figure 2). The results above revealed that the dye had to be tightly bound to the zeolite via cavity and channel prior to an effective degradation.

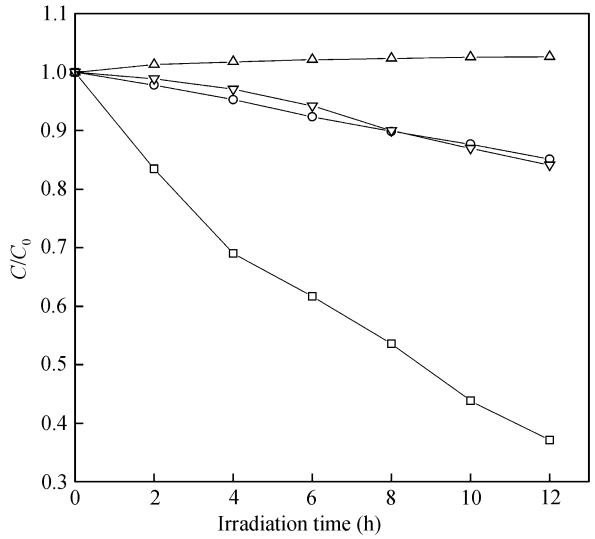


Figure 2 Photooxidation of different substrates mediated by different zeolites. □, MG/NaY; ○, Rh6G/NaY; ▽, MG/ZSM-5; △, Rh6G/ZSM-5. [dyes] = 2×10^{-5} mol·L^{-1}; [zeolites] = 1.5 mg/50 mL; [H_2O_2] = 2×10^{-4} mol·L^{-1}.

Moreover, it was also found both pure Al_2O_3 and MCM-41 without Al could not oxidize MG (Figure 3). NaY (Si/Al=2.4) was shown to have an obviously higher activity than NaY (Si/Al=3.7) for the oxidation of MG. Hence, it is confirmed one more time that the Al present in the oxygen tetrahedron of zeolite plays an important role in the activity of zeolite. To test the effects of exchangeable cation in the zeolite, the zeolites with different exchangeable cation, such as FeY and HY, derived from NaY were prepared. It was observed that both FeY and HY could activate H_2O_2 to effectively oxidize MG under visible light irradiation (Figure 4). Among these Y-type zeolites, the visible-light-driven activities for MG oxidation are in order of NaY>FeY>HY. Our results indicate that it is the intrinsic property of zeolite Y and not loaded exchangeable cations inside zeolite Y that is responsible for H_2O_2 decomposition.

Oxidation of other dyes was also carried out. Similar to MG, the cationic dyes, Fuchsin basic, Methyl violet, and Thionine, were oxidized efficiently (Figure 5). Cationic dyes with larger molecular size, such as Rh6G, were oxidized slowly. On the contrary, both anionic dyes, such as Orange Ⅱ, and colorless cationic compounds, such as benzyltrimethylammonium chloride, could not be oxidized (H_2O_2 was not decomposed, either) under the same conditions. Thus, oxidation of substrates mediated by zeolite should need two crucial factors. One is that the substrate (the whole or part of the molecule)

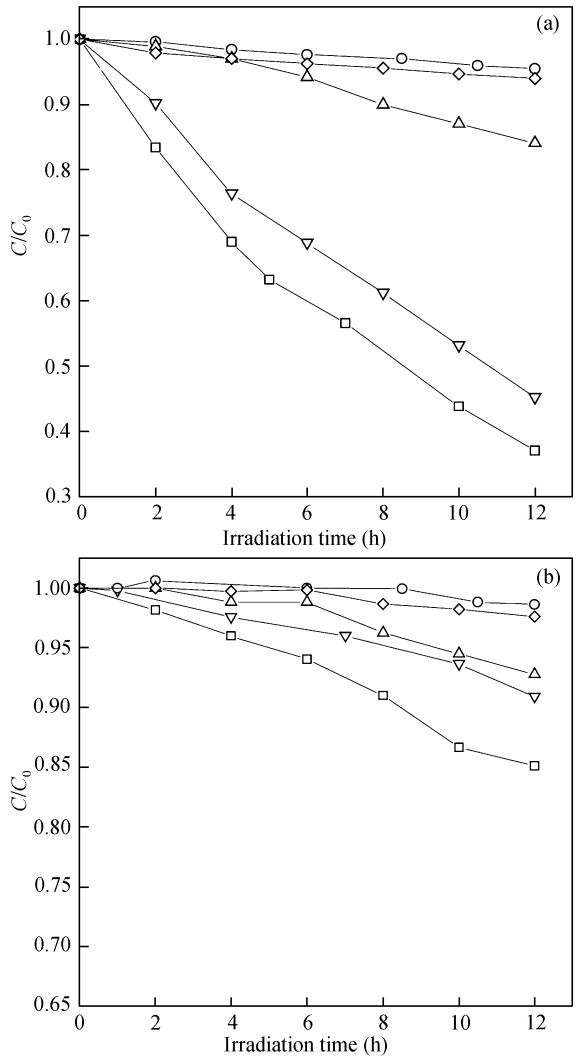


Figure 3 (a) Photooxidation of MG mediated by different zeolites; (b) decomposition of H_2O_2 mediated by different zeolites. □, NaY (Si/Al=2.4); ▽, NaY (Si/Al=3.7); △, ZSM-5; ○, MCM-41; ◇, Al_2O_3. [MG] = 2×10^{-5} mol·L^{-1}; [zeolites] = 1.5 mg/50 mL; [H_2O_2] = 2×10^{-4} mol·L^{-1}.

with positive charges must pass the aperture to be tightly bound to zeolite. Another, substrate should have the capability to absorb visible light.

A focus is what H_2O_2 is initially converted to in the system. As a good single electron shuttle, H_2O_2 can either produce $^{\bullet}$OOH as reductant, or produce $^{\bullet}$OH as oxidant. Spin-trapping ESR, a useful method to detect active radicals, such as $^{\bullet}$OH and $^{\bullet}$OOH, was used to examine H_2O_2 decomposition pathway in the system[10]. Under *in situ* laser light irradiation (λ = 532 nm), characteristic quartet peaks of DMPO-$^{\bullet}$OH adducts appeared gradually in the aqueous MG/NaY/H_2O_2 system, and the intensity increased with irradiation time (Figure 6(a)). No ESR signal was detected when NaY or MG was ab-

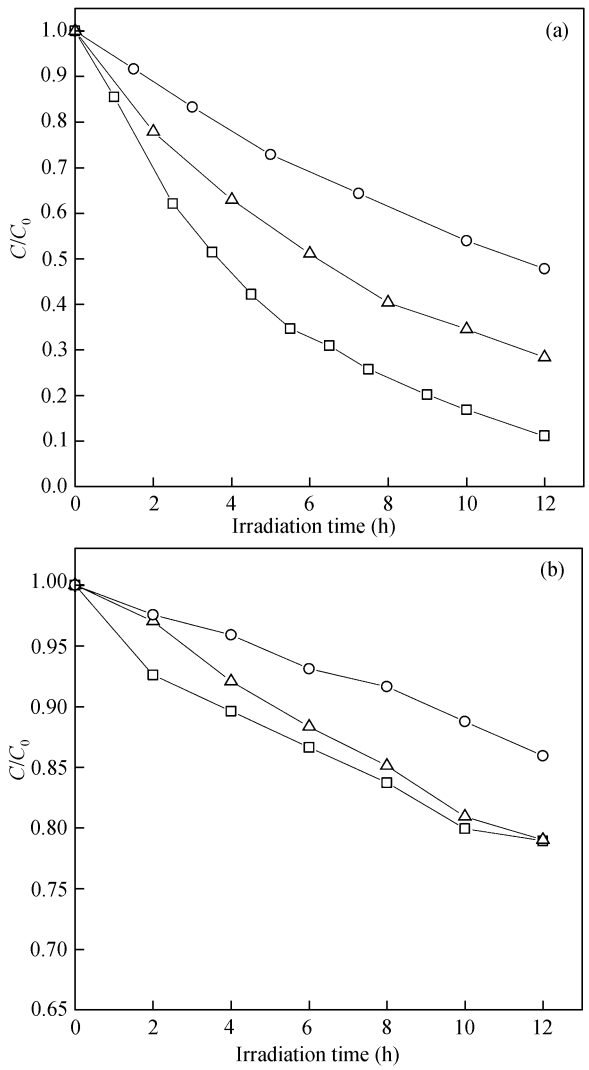


Figure 4 (a) Photooxidation of MG mediated by different zeolites; (b) decomposition of H_2O_2 mediated by different zeolites. □, NaY; △, FeY; ○, HY. [MG] = 2×10^{-5} mol·L^{-1}; [NaY], [FeY] or [HY] = 1.5 mg/50 mL; [H_2O_2] = 2×10^{-4} mol·L^{-1}.

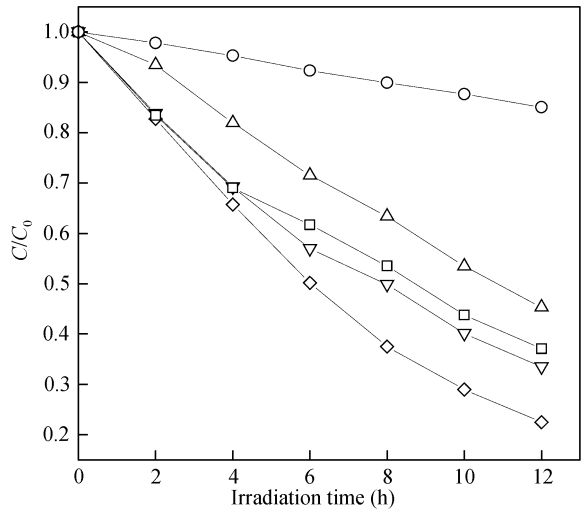


Figure 5 Photooxidation of different dyes. □, Malachite Green; ▽, Fuchsin Basic; △, Methyl Violet; ◇, Thionine; ○, Rhodamine 6G. [dye] = 2×10^{-5} mol·L^{-1}; [NaY] = 1.5 mg/50 mL; [H_2O_2] = 2×10^{-4} mol·L^{-1}.

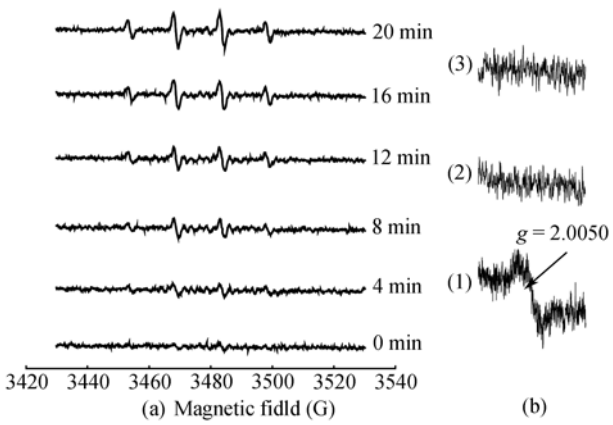
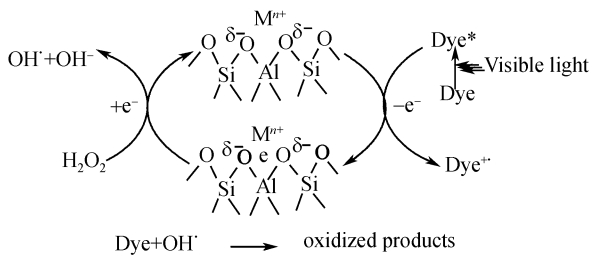


Figure 6 (a) DMPO-$^{\bullet}$OH spin-trapping ESR spectra of H_2O_2/MG/NaY suspending solution. (b) ESR spectra with visible light irradiation (>450 nm) under vacuum at room temperature: (1) MG/NaY; (2) MG/Al_2O_3; (3) MG/SiO_2.



Scheme 2 Proposed mechanism for the oxidation of MG with H_2O_2 assisted by NaY under visible light irradiation.

sent under irradiation. We also tried to observe the DMPO- $^{\bullet}$OOH/$O_2^{\bullet-}$ adducts. However, no signal of DMPO- $^{\bullet}$OOH/$O_2^{\bullet-}$ adducts appeared. Therefore, H_2O_2 decomposition in the system was highly selective to produce $^{\bullet}$OH radicals, not like Fenton reaction, in which both $^{\bullet}$OH and $^{\bullet}$OOH/$O_2^{\bullet-}$ radicals are generated.

Previous studies showed that zeolite could trap electrons from suitable substrates and stabilize the radical cations in photoreaction[7,11−14]. Thomas et al. reported photolysis of anthracene- or pyrene- impregnated alkali-metal-cation-exchanged zeolite X and Y with a nitrogen laser (337 nm) and the charge-balancing cations in zeolites as electron acceptors in photoinduced processes[13,15]. Here, we found that an obvious signal (g = 2.0050) appeared from ESR spectra when the solid powder of NaY zeolite loading dye was irradiated by visible light, suggesting the zeolite accepted an electron from the excited dye (Figure 6(b)). When H_2O_2 was

added to the system, the signal of the single electron disappeared immediately, resulting in the production of $^{\bullet}OH$ radicals. On the basis of our experimental results, we believe that the dye in zeolite is excited by visible light and then transfer electron to the zeolite. The surplus electron trapped in the zeolite moiety can easily transfer to H_2O_2 to generate $^{\bullet}OH$ radicals that can render MG to de-N-methylation, dearylation, and hydroxylation (Table 1). A possible pathway for the efficient activation of H_2O_2 inside NaY zeolite is proposed (Scheme 2).

3 Conclusions

This work reveals that zeolite NaY trapping dyes can efficiently decompose H_2O_2 into $^{\bullet}OH$ radical to oxidize the dyes under the visible light irradiation. Although the reaction TON is relatively low at the present stage, it is expected that zeolite will become a more efficient photocatalyst for use of H_2O_2 in selective oxidation in water via readily controlling its space and composition in future studies.

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