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Photochemical production or depletion of hydrogen peroxide controlled by different electron transfer pathways in methyl viologen intercalated clays

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Abstract

The composites prepared by intercalating methyl viologen (MV^{2+}) into clay lamella could lead to either production or depletion of hydrogen peroxide (H_2O_2) under UV light irradiation. H_2O_2 was found to be generated in aerated aqueous dispersion of Laponite intercalated with MV^{2+} (MV^{2+}–Lap). In contrast, MV^{2+} intercalated Nontronite (MV^{2+}–Non), promoted the decomposition of H_2O_2. In both cases, the intercalated MV^{2+} was excited upon UV irradiation and then captured an electron from clay hosts, through which methyl viologen cation radical ($MV^{+\bullet}$) was formed. In iron free Lap, $MV^{+\bullet}$ reduced the dissolved oxygen to superoxide/hydroperoxie radicals ($O_2^{-\bullet}/HO_2^{\bullet}$) and H_2O_2 was produced via self-disproportionation. When iron species were present in clay host, however, $MV^{+\bullet}$ reduced structural Fe(III) to Fe(II) in clay lattice, leading to the decomposition of H_2O_2.

Keywords: Hydrogen peroxide; Clay minerals; Methyl viologen

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1. Introduction

Clay minerals play important roles in the transfer and transformation of chemicals in environment and are used widely as industrial catalysts [1–4]. The framework of clays are negatively charged silicate layers which are able to accommodate positive charged species, such as metal complexes and organic cations. Not only the geometry and assemblies of the guest species within clay sheets differentiate considerably from that in homogeneous phases, also their physiochemical properties are altered due to the special microenvironment in clay. Moreover, various constitutes of clays have been found to act as electron acceptors and/or donors for particular compounds [3–7]. Many photochemical systems constructed of clay and photoreactive species were designed to achieve effective donor–acceptor electron transfer and charge separation. Recently, clay minerals were evidenced to donate electrons to excited methyl viologen (MV^{2+}) and the electron donating sites were assumed to be bridging Si–O–Al oxygen or crystal edge of clays [8]. In the present study, it was found that composites of MV^{2+} and clays could either produce H_2O_2 from dioxygen or promote the decomposition of H_2O_2. $MV^{+\bullet}$ was generated in both systems, which reduces dissolved molecular oxygen to $O_2^{-\bullet}/HO_2^{\bullet}$ (iron free clay) or structural Fe(III) to structural Fe(II) (iron containing clay), leading to the generation or depletion of H_2O_2.This result provides further understanding on the electron transfer pathway within clay–MV^{2+} systems.

2. Experimental

2.1. Chemicals

Horseradish peroxidase (POD) was purchased from Huamei Biologic Engineering Co. (China). *N*,*N*-diethyl-*p*-phenylenediamine (DPD) was from Sigma. Methyl viologen was from Acros. H_2O_2, trisodium citrate, sodium bicarbonate, sodium dithionate, hydrochloric acid and 1,10-phenanthroline were of reagent grade and used without further purification. Barnstead UltraPure water (18.3 MΩ) was used throughout the study.

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2.2. Minerals

Laponite (Lap) and Nontronite (Non) were kindly provided by Dr. H.Y. Zhu, Australian Key Centre of Microanalysis & Microscopy and School of Chemistry, The University of Sydney. Laponite was synthetic magnesiansilicates with high purity and was used as received. Non was a kind of natural clay minerals which contains Fe(III) in its octahedral lattice. Raw Non was pre-treated with trisodium citrate and sodium dithionate in sodium bicarbonate solution at 80 °C (CBD method, which only removes trace iron oxides but not iron in the octahedral lattice) [9], followed with hydrogen peroxide to remove organics impurities [10]. Then it was thoroughly washed with deionized water and air dried. The content of total iron in Non was about 20%, as determined by JT-ULTIMA inductively coupling plasma–atomic emission spectra (ICP-AES) after digestion by concentrated acid.

The MV^{2+}–clay composites were prepared according to literature [8]. Briefly, clays were dispersed in aqueous MV^{2+} solution (the amount of MV^{2+} was equal to the cation exchange capacity of each clay), and the suspensions were stirred for 24 h. Then they were thoroughly washed and freeze dried. The obtained samples were named as MV^{2+}–Lap and MV^{2+}–Non, respectively.

2.3. Procedure and analysis

X-ray diffraction patterns of the samples were recorded on Regaku D/Max-2500 diffractometer under Cu Kα radiation. The electron paramagnetic resonance (EPR) signals of MV^{2+}–clay powder were recorded at ambient temperature on a Brucker E500 spectrometer. Light source was a 500 W Xe lamp. The settings for the EPR spectrometer were: center field, 3480 G; sweep width, 100 G; microwave frequency, 9.78 GHz; modulation frequency 100 KHz; power 12 mW.

The reaction systems containing 0.2 g/L clay sample (pH was adjusted to 5.0 ± 0.1) were irradiated by a 100 W Hg lamp (Toshiba SHL-100UVQ-2). At given time interval, about 5 mL aliquot was sampled and centrifuged. The concentration of H_2O_2 in the supernatant was determined spectrophotometrically by the DPD method [11] on a Hitachi U-3100 spectrophotometer.

3. Result and discussion

3.1. Characterization of MV^{2+}–clay composite

The X-ray diffraction pattern of each sample is displayed in Fig. 1 and the distance between clay sheets (*D*) was calculated from the peak position. All samples showed characteristic d_{001} peak except for Lap due to the poor long range order of its platelets. *D* value of original Non was 0.98 nm, which is close to the values for dehydrated smectites [8]. Galley height of MV^{2+}–Non and MV^{2+}–Lap was 1.29 and 1.30 nm. The expansion in interlayer space of clay host not only confirmed the intercalation of MV^{2+}, but also suggested that the plane of MV^{2+} molecule was paralleled to clay sheet because the thickness of pyridine ring (0.3 nm) was close to the increase in *D* value.

3.2. Photo production of H_2O_2

H_2O_2 is a powerful and environmentally benign oxidant that is widely used in the organic synthesis and contaminants removal. Many reaction systems containing MV^{2+} have been developed to produce hydrogen peroxide, in which MV^{2+} acts as the electron shuttle between electron donor and molecular oxygen [12,13]. In the aerated dispersion of MV^{2+}–Lap, about 12 μM H_2O_2 was accumulated within 8 h of UV light irradiation (Fig. 2). Further investigation demonstrated that both MV^{2+} and Lap are necessary for this reaction because very little amount of H_2O_2 was produced in irradiated system contained only Lap or

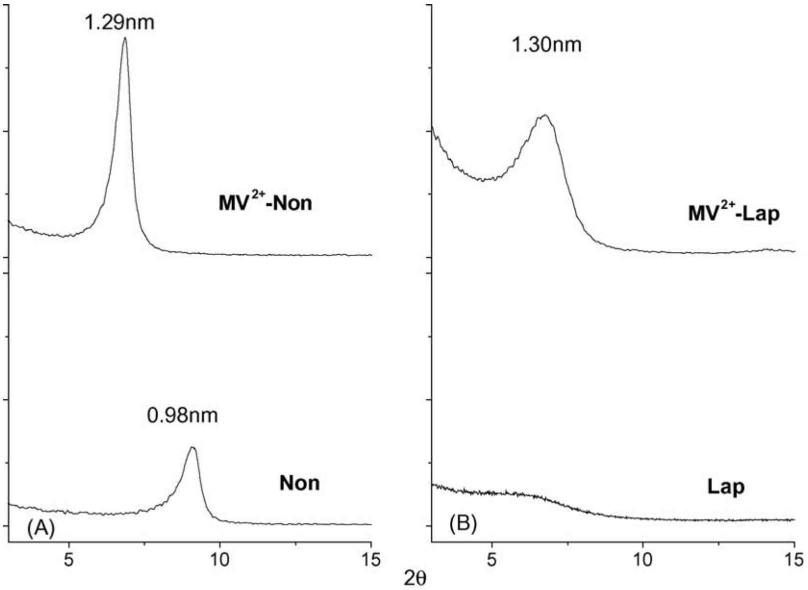


Fig. 1. XRD patterns of: (A) Non, MV^{2+}–Non and (B) Lap and MV^{2+}–Lap.

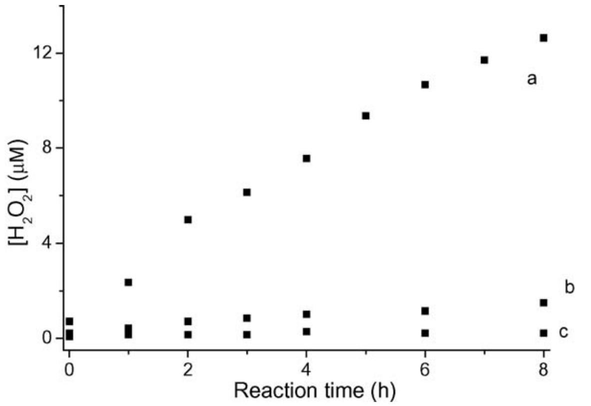


Fig. 2. Production of H_2O_2 at pH 5.0 in: (a) dispersion containing 0.2 g/L MV^{2+}–Lap, (b) MV^{2+} aqueous solution and (c) dispersion containing 0.2 g/L Lap.

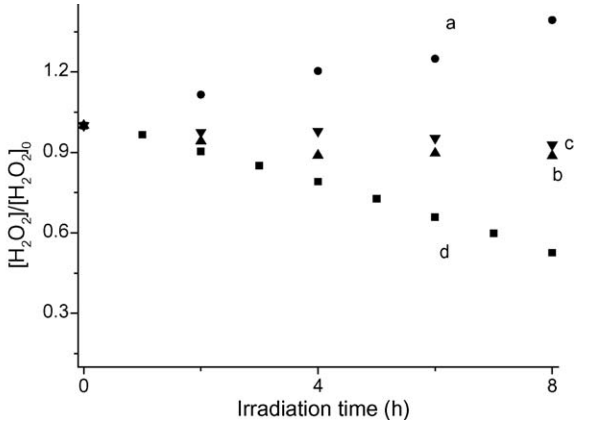


Fig. 4. Variation in H_2O_2 concentration ($[H_2O_2]_0 = 40$ μM) in the presence of 0.2 g/L: (a) 0.2 g/L MV^{2+}–Lap, (b) 0.2 g/L Non, (c) 1×10^{-4} M MV^{2+} and (d) 0.2 g/L MV^{2+}–Non at pH 5.0.

1×10^{-4} M MV^{2+}. (It was evidenced that about 50 μM MV^{2+} can be adsorbed on 0.2 g/L Lap, therefore, MV^{2+} concentration in MV^{2+}–Lap dispersion was less than 1×10^{-4} M.) Considering the electron donating ability of Lap, it was supposed that excited MV^{2+} was reduced to $MV^{+\bullet}$ by electron rich sites in clay framework. Then $MV^{+\bullet}$ induced the formation of H_2O_2 via O_2 reduction. Fig. 3 showed that with 3 h UV irradiation of MV^{2+}–Lap powder under vacuum condition, a symmetric signal with $g = 2.005$ and a peak to peak line width of 8 G appeared, which is the typical ESR signal of $MV^{+\bullet}$ [8]. After exposure to air, the intensity of signal gradually decayed due to the electron transfer from $MV^{+\bullet}$ to molecular oxygen. It is worth to be mentioned that when H_2O_2 was present initially in dispersion of MV^{2+}–Lap, its concentration also increased with UV irradiation, indicating that the generated $MV^{+\bullet}$ prefer to reduce dioxygen than react with H_2O_2 (Fig. 4, curve a).

3.3. *Photoinduced depletion of H_2O_2 assisted by MV^{2+}–Non*

Whereas Non contains electron rich Si–O–Al oxygen, little H_2O_2 was produced from aerated dispersion, and $MV^{+\bullet}$ was not detected in its powder under UV light irradiation (data not shown). This was attributed to structural Fe(III) in Non, which may quench MV^{2+} excited state ($[MV^{2+}]^*$) and cut off the following electron transfer route by which H_2O_2 is produced. On the contrary, numerous studies have shown that the various iron species, such as goethite and green rust, contribute to the loss of H_2O_2 in natural systems [14–16], while structural iron (III) in clay lattice showed poor activity to catalyze this reaction under UV light irradiation (Fig. 4, curve b). The decrease in H_2O_2 concentration in aqueous MV^{2+} solution was also neglectable (curve c). However, MV^{2+}–Non could promote obviously the decomposition of H_2O_2 (curve d).

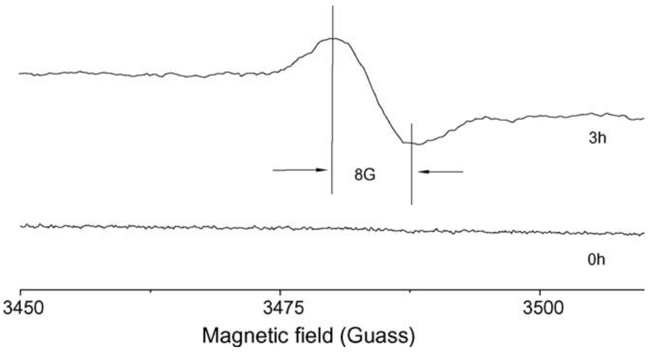
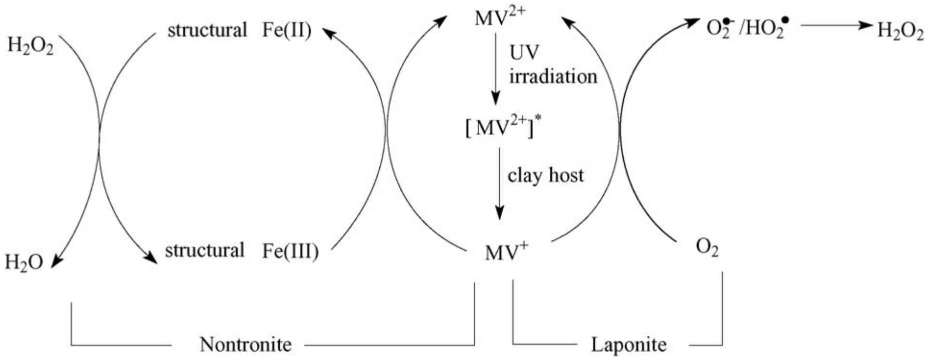


Fig. 3. ESR spectra of MV^{2+}–Lap before and after irradiation.

Early investigations on the iron catalyzed decomposition of H_2O_2 confirmed that the pivotal step in the overall reaction is the reduction of Fe(III) to Fe(II) because Fe(II) species show much higher reactivity than Fe(III) species do [14,16]. For instance, ferric ions and iron oxides can form surface complexes with hydroxyl group (≡Fe(III)-OH) or deprotonated hydrogen peroxide (≡Fe(III)-OOH), both of which are photoreactive and generate surface Fe(II) upon UV irradiation [17–20], thus they can efficiently catalyze the decomposition of H_2O_2. To understand the origin of reactivity difference between Non and MV^{2+}–Non, production of Fe(II) was examined in aqueous suspensions of each sample according to the following procedure: 10 mg clay samples were dispersed in 5 mL water. The deaerated dispersions (purged with argon) were stirred for 3 h under Hg lamp irradiation. Then 5 mL HCl (1 M) free of oxygen was added and the resulting suspension (1 g/L clay and 0.5 M HCl) was allowed to react for 1 h to extract iron in the clay samples [2]. The concentration of Fe(II) and total iron (Fe(t)) was determined in the upper supernatant after centrifugation by 1,10-phenanthroline method. As displayed in Table 1, with 3 h UV irradiation, the Fe(II) percentage in HCl extract of Non was less than 1%. The low Fe(II) production is attributed to the special site of iron in clay: structural Fe(III) is restricted in the octahe-

Table 1
Fe(II) and Fe(t) concentration in HCl extraction of Non and MV^{2+}–Non after 3 h UV irradiation

Sample	Fe(II) (μM)	Fe(t) (μM)	Fe(II)/Fe(t)(%)
Non	0.5	59.0	0.8
MV^{2+}–Non	11.5	55.6	20.6



Scheme 1. Proposed electron transfer pathways in MV^{2+}–clay composites.

dral lattice sandwiched by two silica tetrahedral sheet and it has little possibility to form photoreactive complexes with OH^- or HO_2^- groups. In contrast, the Fe(II) percentage in MV^{2+}–Non extract was about 20%. Previous studies have reported that reduction of structural Fe(III) to Fe(II) in clay could induce the rapid decompose of H_2O_2 [21,22], therefore the higher reactivity of MV^{2+}–Non was ascribed to the photogenerated structural Fe(II).

The generation of Fe(II) in MV^{2+}–Non system indicated that $MV^{+\bullet}$ was generated upon UV irradiation and acted as the reductant for structural Fe(III). This process is energetic favorable taking into account of the redox potential of structural Fe(III) and $MV^{+\bullet}$ (0.44 and −0.45 V respectively) [23,24]. It was assumed that MV^{2+} transformed to $MV^{+\bullet}$ via capturing electrons from bridging Si–O–Al oxygen in Non. Since $MV^{+\bullet}$ was sandwiched by clay sheets, the reaction of it with structural Fe(III) is faster than that with dissolved molecular oxygen, resulting in the production of structural Fe(II), and further, the decomposition of H_2O_2.

The electron transfer pathways in MV^{2+}–clay composites are summarized in Scheme 1 based on the above experimental results. The intercalated MV^{2+} is excited by UV irradiation and then captures electrons from clay hosts, forming $MV^{+\bullet}$. In iron free Lap, $MV^{+\bullet}$ rapidly reduces dissolved molecular oxygen to $O_2^{-\bullet}/HO_2^{\bullet}$, subsequently, H_2O_2 was produced. When Fe(III) is present in clay, however, it is reduced to Fe(II) by $MV^{+\bullet}$, leading to the decomposition of H_2O_2. Our work indicated that as potential electron donor to the photoreactive guest species in their interlayer, clays could induce either production or depletion of hydrogen peroxide, controlled by different electron transfer pathways. Such performance motivates us to design more clay based photochemical systems to achieve desired chemical processes.

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