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Iron Oxychloride (FeOCl): An Efficient Fenton-Like Catalyst for Producing Hydroxyl Radicals in Degradation of Organic Contaminants

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Supporting Information

ABSTRACT: An iron oxychloride (FeOCl) catalyst was developed for oxidative degradation of persistent organic compounds in aqueous solutions. Exceptionally high activity for the production of hydroxyl radical (OH·) by H_2O_2 decomposition was achieved, being 2−4 orders of magnitudes greater than that over other Fe-based heterogeneous catalysts. The relationship of catalyst structure and performance has been established by using multitechniques, such as XRD, HRTEM, and EPR. The unique structural configuration of iron atoms and the reducible electronic properties of FeOCl are responsible for the excellent activity. This study paves the way toward the rational design of relevant catalysts for applications, such as wastewater treatment, soil remediation, and other emerging environmental problems.

The generation of oxygen-containing radicals, more generally known as reactive oxygen species (ROS), is an important process in nature, occurring from the human body to the nebular of outer space.[1] Hydroxyl radicals (HO·), as one of the most powerful oxidants, play a dual role as both deleterious and beneficial species.[2] In particular, the supreme oxidation potential of HO· makes it a strong oxidant for water treatment, soil remediation, biological sensors, and material synthesis.[3]

Nowadays, the ever-growing contamination of the surface or underground water due to industrialization has abstracted a great deal of attention. Especially, a series of nonbiodegradable or persistent organic compounds adversely affects the quality of human life through food chains or environmental cycles.[4] The development of novel processes to generate HO· is highly desired for the environmental remediation, especially purifying drinking water containing low-level micropollutants.[5] Among all approaches, the conventional Fenton reagent composed of hydrogen peroxide (H_2O_2) and ferric ion (Fe^{2+}) has long been applied for the production of HO·.[6] It is a primary cornerstone for the biodegradation.[7]

However, several drawbacks of the current Fenton process limit the scale-up of its application, including the narrow pH range for reaction (pH = 2.5−3.5) and the accumulation of iron-containing sludge, which is regarded as a secondary pollution and the loss of catalyst. Except for iron, other transitional metals or nonmetallic materials,[8] including manganese, copper, cobalt, cerium, gold, and carbon exhibit catalytic activities for the Fenton reaction. On the other hand, photo-, sono-, or electro-assisted Fenton reactions, or to say, a family technique, have been widely studied as well.[9] Compared to homogeneous Fenton systems, heterogeneous Fenton systems have proven to be promising alternatives because of its easy separation. In order to simplify the process and overcome the secondary pollution, the developed heterogeneous catalysts should be recyclable in a broad pH range (pH = 3.0−9.0). However, there are two great challenges for heterogeneous Fenton catalysts: (i) lower activities in yielding OH· compared to the conventional homogeneous Fenton reagent; (ii) the poor stability of the catalysts because of serious leaching of active metals in the operation.[10] Therefore, the key problem is how to design heterogeneous Fenton-like catalysts, which can effectively generate HO· by H_2O_2 decomposition with high durability.

Here we first report a new Fenton-like catalyst, iron oxychloride (FeOCl), which exhibits supreme efficiency for yielding OH· by H_2O_2 decomposition and exceptional performance in the degradation of persistent organic compounds. Actually, FeOCl was reported as a functional material decades ago.[11] The structure of FeOCl is characteristic of its self-stacked crystallographic gap, called "van der Waals layer" (Scheme S1). FeOCl has proven to be an excellent inorganic host for intercalation reaction due to the weak interactions between the layers.[12] The proper modification of this structure, arising from the strong oxidizing power, will change the chemical state of iron ($Fe^{3+} \rightarrow Fe^{2+}$) by transferring charge between the intercalated organic compounds and the inorganic matrix.[13] About 25% Fe^{3+} was demonstrated to be "in situ" reduced to Fe^{2+} when the guest molecules were adsorbed or interacting with FeOCl.[13b,c]

In this work, FeOCl was prepared using a chemical vapor transition method.[13c] The detailed procedure can be seen in Supporting Information (SI). During this process, the solid hematite was reacted with the anhydrous $FeCl_3$, which was gasified at above ∼588 K. The formation of FeOCl was supposed to occur through structural rearrangement and recrystallization within 40 h.

The performance of the as-prepared catalyst was evaluated by degrading several model pollutants. Phenol is a common model compound for the advanced oxidation process and also an important intermediate for the degradation of aromatic hydrocarbons with higher molecule weight.[14] 2,4,6-nitro-benzene was used as the typical organic nitrogen compounds.

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Benzoic acid, ethylbenzene, and quinoline are common occurring contaminants in the wastewater from coal chemical plants.[15] In addition, tricholoroethane and trichloroethylene are chlorinated solvents, leading to serious environmental concerns in underground water;[16] bisphenol A (BPA), methylene blue, and amoxicillin were model contaminants as endocrine disruptor,[17] azo dye, and antibiotics,[18] respectively.

Since the conventional Fenton reaction is quite sensitive to the pH value of the system, a detailed comparison of the catalytic performance under different initial pH values was shown in Figure S3 by the degradation of BPA. As previously reported, BPA and its degradation products did not influence the pH value of the solution.[19] Thus we can safely rule out the employment of buffer solutions. The degradation rate of BPA was decreased with an increase in pH value. Complete oxidation was reached within 30 min with pH <4. In addition, BPA degradation was proved to be favored at higher temperatures in a range of 283−333 K (Figure S4).

As listed in Table 1, all the aromatic compounds (initial 100 ppm) were completely oxidized companying with a ∼50% conversion of H_2O_2. The initial concentration of ethyl-benzene was lower than 100 ppm due to its low solubility. The conversions of tricholoroethane and trichloroethylene were above 90%. However, the degradation of methyleneblue and amoxicillin was obviously quenched, perhaps because of the strong scavenge of OH· by their intermediates.[20] A blank test without addition of organic compound was also carried out, and the decomposition of H_2O_2 was strongly depressed (conv. 12.3% within 30 min, Figure S5). This indicates the existence of surface reactions between OH· and other free radicals or the solvent, which hamper the further decomposition of H_2O_2.

Table 1. Degradation of Various Robust Organic Compounds[a]

entry	contaminants	initial conc. (ppm)	time (min)	conv.[b] (%)	H_2O_2 conv. (%)
1	phenol	100	30	100.0	52.0
2	benzene	100	30	100.0	55.6
3	benzoic acid	100	30	100.0	48.3
4	ethylbenzene	60	30	100.0	33.2
5	quinoline	100	30	100.0	50.1
6	2,4,6-nitrobenzene	132	30	100.0	61.3
7	bisphenol A	113	30	100.0	50.0
8	trichloroethane	63	30	90.1	36.6
9	trichloroethylene	113	30	93.6	39.9
10	methylene blue	80	30	21.1	–
11	amoxicillin	100	30	23.3	–
12[c]	–	–	30	–	12.3

[a]Blank test without the loading of FeOCl was shown in Table S2 [b]Reaction conditions: initial $[H_2O_2]$ = 530 ppm, 313 K, pH = 4.0, 200 mg/L of catalyst. The conv. represented the destruction of each organic compound. [c]Blank test without organic compound dosing.

DMPO-trapped EPR spectra were used to demonstrate the generation of OH· Han et al. has proven that the steady state of HO· could reach within 120 s in the case of homogeneous Fenton reaction.[21] So, it is rational to compare the steady-state concentration of HO· as well. The detailed procedure for the measurement can be seen in SI. The EPR spectrum of the DMPO−OH· adduct generated from as-prepared FeOCl and the conventional Fenton reagent (Fe^{2+} ion) are shown in Figure 1a. A higher amount of OH· was trapped in the case of the as-prepared FeOCl in the first 120 s. Due to the hyperfine interaction between the electron spin of OH· and the orbital spin of N atom in DMPO, the EPR signal was split into four single lines with a spacing of 14 G in the magnetic field. The *g* factor of each line was 2.0198, 2.0112, 2.0027 and 1.9941, respectively, corresponding to an intensity ratio of 1:2:2:1. Since the identical sample tubes were placed in the resonant cavity, the volume of the solution containing DMPO adducts and the concentration of DMPO were the same for both cases. The line shape of the DMPO adduct was of the same mode as well as the line width of each signal. Therefore, the intensity of the EPR signal is dependent on the OH· concentration generated by each catalyst. We conclude that the steady-state concentration of OH· over FeOCl is higher than that of homogeneous Fenton catalyst.

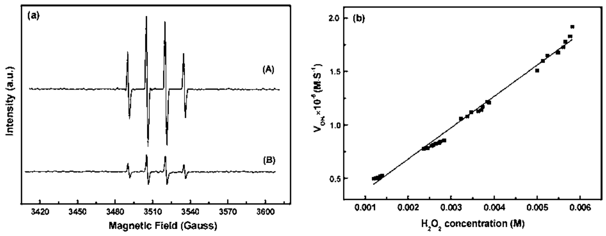

Figure 1. (a) DMPO trapped electron paramagnetic resonance spectra (EPR) at 120s over FeOCl (A) and conventional Fenton reagent, Fe^{2+}(B). (b) Formation rates of OH· as a function of H_2O_2 concentration over FeOCl.

The durability of FeOCl was tested by recovering the solid catalyst through filtration. The remains were washed with DI water at neutral pH and reused in the following cycle. The catalytic performance for 5 cycles is shown in Figure S6a. The residue content of iron in the solution after each cycle was in the range 0.57−1.25 ppm, which was below the limitation of Fe in EU and US (<2 ppm). The potential contribution of homogeneous Fe ions (usually more than 20 ppm) to the catalytic reaction is negligible. Meanwhile, the Cl^- concentration in the range 1.03−1.62 ppm was also obtained, being close to the leaching of Fe. The recovery of FeOCl after 5 cycles calculated based on the leaching amount of Fe or Cl ions was above 96.6% (Figure S6b).

The rate for the generation of OH· was measured following a modified molecule probe method (experimental details and calculation methods given in SI).[22] As shown in Figure 1b, the OH· generation rate constant over FeOCl was as high as 2.93×10^{-4} s^{-1}, which was 1−3 orders of magnitude higher than other iron-containing materials, such as goethite (α-FeOOH), hematite (α-Fe_2O_3), and ferrihyrite ($Fe_5HO_8 \cdot 4H_2O$) (Table 2). When the rate constant was normalized to the unit surface area, it was more than 10 000 times higher than that for α-Fe_2O_3. The turnover frequency (TOF) for FeOCl, based on the unsaturated coordinated iron atoms on the exposure surface, was about 1.46 s^{-1}.

A typical X-ray diffraction pattern of FeOCl (Figure S7) was indexed within 10 peaks (JCPDS card no. 24-1005). The lattice parameters of FeOCl were calculated to be *a* = 3.7715 Å, *b* = 7.9117 Å, and *c* = 3.3026 Å. The catalyst structure was characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAD). A flat-like morphology can be observed in SEM and TEM images (Figure 2a,b) with 0.3−10 μm in length and 100−300 nm in thickness for all particles. A typical HRTEM image (Figure 2d) showed that the

Table 2. Comparison of OH· Formation Rates for Different Iron-Containing Materials

material	TOF (s^{-1})	$k_{OH\cdot}$ (s^{-1})	$k_{OH\cdot,surf}$ ($g\cdot s^{-1}\cdot m^{-2}$)	ref
α-Fe_2O_3	–	4.00×10^{-7}	8×10^{-9}	23b
α-FeOOH	–	4.25×10^{-5}	1×10^{-7}	23b
$Fe_5HO_8\cdot 4H_2O$	–	2.00×10^{-5}	1×10^{-7}	23b
FeOCl	1.46	2.93×10^{-4}	3.67×10^{-5}	this study
Fe^{2+a}	1.25×10^{-3}	2.5×10^{-4}	–	22a
Fe^{2+a}	6×10^{-3b}	–	–	22a

[a] $FeClO_4$ was used as the homogeneous Fenton catalyst. [b] Initial TOF based on the initial generation of OH· was listed here.

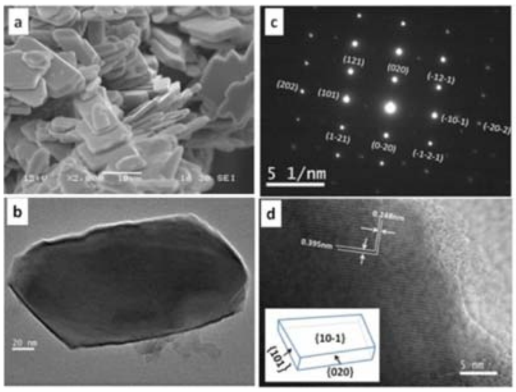

Figure 2. Morphology of the as-prepared FeOCl; (a) SEM, (b) TEM, (c) SAD, and (d) HRTEM.

lattice distances were 0.248 and 0.395 nm, respectively, which were close to those exhibited by SAD (Figure 2c). It indicated that a basal plane (10−1) was enclosed by {101} and {020} facet as the vertically aligned plates. The specific surface area (7.99 m^2/g) of FeOCl was measured by N_2 adsorption (Figure S8). The surface terminations of FeOCl at [020] and [101] direction are depicted as Schemes S2 and S3, respectively.

A generally accepted point for the mechanism of homogeneous Fenton reaction is: (i) The ferrous and ferric ions were first hydrolyzed and coordinated by water molecule; (ii) $Fe^{(II/III)}$-hydroperoxy complexes were formed in the presence of H_2O_2; (iii) OH· was formed through the unimolecular decomposition of hydroperoxy complexes. The formation and decomposition of iron-hydroperoxy complex were the trigger steps of the homogeneous Fenton reaction;[23] (iv) the chain reaction is propagated by various reactions between ferrous/ferric ion and ROS and terminated by the recombination of radicals.[24] Of all these elemental reactions, the decomposition of iron-hydroperoxy complex was proposed to be the rate-determining step, which greatly impacted on the productivity of free radicals.[25] By optimizing the operational parameters, an ideal performance of homogeneous Fenton system was obtained at pH = 3 and a ratio of $[H_2O_2]_0/[Fe(III)]_0$ above 500.[25a]

To date, the mechanism study for the heterogeneous Fenton reactions is very limited. Kwan et al.[22b] demonstrated that the decomposition of H_2O_2 and the degradation of organic compounds mainly occurred on the iron oxide surface. Smirnov et al.[26] found that specific catalytic sites in a nanosized γ-Fe_2O_3 surface were at least 50-fold more effective in OH· production than ferric ions. The catalytic performance varied remarkably with changes in the crystalline phases of solid iron materials. Of all iron (hydr)oxides, goethite (α-FeOOH) showed the best performance for the generation of OH·.[27]

As listed in Table 2, the rate for OH· generation over FeOCl was higher by 2 orders of magnitudes than that for α-FeOOH. The exceptionally catalytic performance of FeOCl is assumed to its unique structure. On the basis of FeOCl structure, a great number of unsaturated iron atoms were exposed at the plane (020), which is the so-called polar surface with a 10.96 atom/nm^2; <4.6 atom/nm^2 was detected for iron(Fe^{III}) oxide or iron hydroxide.[28] A common viewpoint is that hydroxyl groups on the polar surface act as active sites, which involved in various physichemical process, such as dissolution, complexation, and anions adsorption.[29] Meanwhile, the iron atom on this facet was posed orderly into a linearship configuration [O−Fe−Cl]. The oxo-bridged configuration ($[Fe-O-Fe]^{4+}$) has been considered to be more efficient in photoinduced Fenton reaction by femtosecond laser spectroscopy.[30] On the other hand, Fe^{III} in FeOCl has proven to be easily reduced to Fe^{2+} when intercalating or reacting with other species.[13b,c] The reduction of Fe^{III} ($Fe^{3+}\rightarrow Fe^{2+}$) in FeOCl was also evidenced by XPS (Figure S9). Fe^{II} was assumed to play a vital role in production of OH·. The generation rate of OH· over Fe^{2+} was proven higher than that over Fe^{3+} by 3−4 orders of magnitudes.[6b] In comparison with water, H_2O_2, a Lewis base molecule, was evidenced to be much more affinitive to the polarized facet of FeOCl. Besides, owing to the strong oxidizing property of FeOCl, the viable electron/charge transfer from H_2O_2 to FeOCl (eq 1) resulted in partial reduction ($Fe^{III} \rightarrow Fe_{1-n}{}^{III}Fe_n{}^{II}$) during reaction when H_2O_2 and organic molecules were adsorbed (eq 1). The existence of Fe^{II} is responsible for the generation of OH· (eq 2). Then the degradation or oxidation of organic compounds sequentially took place in solution, when the radicals diffused into near surface (eq 3). The self-redox properties of iron atoms in FeOCl induced by H_2O_2 were particularly facile for the generation of OH·. The overall reaction is illustrated by Scheme S4.

$$FeOCl + H_2O_2 \leftrightarrow Fe_{1-n}{}^{III}Fe_n{}^{II} + OOH\cdot + H^+ \tag{1}$$

$$\equiv Fe^{II} + H_2O_2 \leftrightarrow \equiv Fe^{III} + OH\cdot + OH^- \tag{2}$$

$$OH\cdot + \text{compounds} \leftrightarrow \text{intermediates} \leftrightarrow CO_2 + H_2O \tag{3}$$

In summary, the unique structural configuration of iron atoms and the reducible electronic properties of FeOCl are responsible for the excellent activity of Fenton reaction. The high productivity of OH· in this system makes the solid Fenton process a more practical application for water treatment. With the combination of the characterization results of fresh and spent catalysts and the durability test, the structural framework of as-prepared catalyst was not changed during the reaction. Nevertheless, the systematic study of the relationship between the structure of solid Fenton catalyst and the OH· generation efficiency is highly desired. Parameters, such as iron coordination number, crystallinity, particle size, surface area, and surface charge of iron may also impact on the catalytic reactivity. The study of those questions is important for the further design of solid Fenton-like catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and Figures S1−S9 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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