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New Insight on Homolytic Peroxodisulfate Activation by Iron Sulfides and $Fe^{IV}=O^{2+}$ Formation

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Abstract The aim of this study is to further investigate the mechanism of peroxodisulfate (PS) activation by iron sulfide crystals (FeS_x) in the surface-mediated process in the aqueous environment. Various iron sulfide crystals were synthesized through co-precipitation and etch coating methods and screened for the intended use. XRD was employed to elucidate differences in crystal structure. PS activation by the synthesized iron sulfides produced about 70 times more oxidation equivalents than is possible by homolytic PS activation, suggesting that homolytic cleavage and a catalytic pathway contribute significantly. Reactive species generated during PS activation were identified as $SO_4^{\bullet-}$, •OH, and $Fe^{IV}=O^{2+}$. The predominant reactive species varied depending on the crystal structure of FeS_x. The investigation of the PS activation process reveals that FeS_x containing pyrite performed longer-term homolytic PS activation and higher stability compared to troilite and mackinawite.

Keywords: FeS_x, peroxodisulfate, homolytic activation, catalytic properties, crystal structure

1. Introduction

When employing iron sulfide, PS activation has traditionally been attributed to homogeneous reactions of dissolved Fe^{2+} ions from the FeS_x or FeO_x surface, leading to the generation of $SO_4^{\bullet-}$, •OH, or $Fe^{IV}=O^{2+}$. However, recent studies have emphasized the importance of heterogeneous mechanisms, in particular the homolytic cleavage of the O-O bond in PS facilitated by the FeS surface (Sühnholz et al. 2020). This surface-mediated activation not only enhances the generation of $SO_4^{\bullet-}$ but also provides improved stability and reusability of the catalyst.

However, $Fe^{IV}=O^{2+}$ plays a crucial role in non-radical PS activation, offering advantages over radical pathways by reducing interference from water constituents and minimizing harmful by-products. The interplay between $Fe^{IV}=O^{2+}$, $SO_4^{\bullet-}$, and •OH in PS activation, and how different FeS_x crystal structures influence these pathways, needs further investigation.

Despite the progress in this field, there is still a lack of in-depth knowledge about the effect of FeS_x crystals on the generation of the various reactive species during PS activation. The efficiency of PS activation is influenced by the specific crystal structure and surface chemistry of the FeS_x used. Understanding the structure-activity relationships of these minerals is crucial for optimizing their performance in environmental remediation.

2. Results and discussion

2.1. Screening of iron sulfides

We synthesized various FeS_x crystal using different iron salts/magnetite and sulfur source through the methods of co-precipitation and etch-coating. Selecting trichloroethene (TCE) as model pollutant for the optimization of actvie and stable FeS_x crystal.

FeS_x prepared from $NH_4Fe(SO_4)_2$, $(NH_4)_2Fe(SO_4)_2$, or from magnetite ($Fe^{III}_{NH_4}$-S, $Fe^{II}_{NH_4}$-S and Fe_3O_4-S, respectively) perform well in PS activation and simultaneous TCE degradation and show rather low iron leaching. Similiarly, the molar ratios of leached Fe to consumed PS for $Fe^{III}_{NO_3}$-S/PS and Fe^{III}_{Cl}-S/PS systems are less than 0.1, indicating that the heterogeneous reaction plays a significant role in those systems, albeit with the lowest reactivity.

Based on the above findings, $Fe^{II}_{NH_4}$-S and $Fe^{III}_{NH_4}$-S prepared by the co-precipitation method and Fe_3O_4-S from etch coating are selected as ideal "candidates" due to their reactivity and high stability. To find out why these iron sulfides are more suitable for PS activation compared to other iron sulfides, $Fe^{III}_{NO_3}$-S and Fe^{III}_{Cl}-S with low reactivity, and Fe_2O_3-S with medium stability and medium reactivity were selected as "comparison materials" to identify the detailed property differences among them.

2.2. Characterization of iron sulfide crystals

XRD was used to obtain information on the crystallization phases of selected FeS_x. These FeS_x crystals display diffraction peaks corresponding to pyrite FeS_2 in $Fe^{III}_{NH_4}$-S, Fe_2O_3-S and Fe_3O_4-S, troilite FeS in Fe^{III}_{Cl}

-S and $Fe^{III}_{NO_3}$-S, and mackinawite FeS in $Fe^{II}_{NH_4}$-S according to crystal database of Jade 5.0.

2.3. *Identification of reactive species*

According to the higher reactivity of $SO_4^{\bullet-}$ over C_6H_{12} and selectivity over the isotopologue C_6D_{12} than •OH (Kopinke and Georgi 2017; Sühnholz et al. 2020), the kinetic isotope effect (k_{C6H12}/k_{C6D12} = KIE) may be indicative of the radical species dominating the reaction. If the KIE is close to 1.1, •OH is the primary reactive species (Lobachev et al. 2008). If the KIE ≥ 2, $SO_4^{\bullet-}$ is considered to be the dominant active species. As the fitted KIE value in Table 2, in $Fe^{III}_{NH_4}$-S/PS and $Fe^{II}_{NH_4}$-S/PS systems, $SO_4^{\bullet-}$ is primary produced in the entire progress, attributing to KIE of about 2. This suggests that while both pyrite (primary phase in $Fe^{III}_{NH_4}$) and mackinawite (primary phase in $Fe^{II}_{NH_4}$) favor the $SO_4^{\bullet-}$ formation, the instability of mackinawite during PS activation leads to Fe^{2+} dissolution, which might facilitate production of other species. Interestingly, the KIE values of Fe^{III}_{Cl}-S/PS and $Fe^{III}_{NO_3}$-S/PS systems are between 1.1 and 2, suggesting a mixture of $SO_4^{\bullet-}$ and •OH, or additional oxidants.

Table 2. Fitted KIE values.

Sample	$Fe^{III}_{NH_4}$-S	Fe^{III}_{Cl}-S	$Fe^{III}_{NO_3}$-S	$Fe^{II}_{NH_4}$-S	Fe_2O_3-S	Fe_3O_4-S
KIE value	2.00	1.42	1.52	1.92	1.73	1.64

Methyl phenyl sulfoxide (PMSO) was used as a probe to detect $Fe^{IV}=O^{2+}$ as possible oxidant because PMSO undergoes $Fe^{IV}=O^{2+}$-mediated oxidation to form methyl phenyl sulfone (PMSO2) via an oxygen-transfer reaction (Wang et al., 2020).

Figure 1a, shows the slectivity production of $PMSO_2$ in the tested systems. $Fe^{II}_{NH_4}$-S/PS, Fe_2O_3-S/PS and Fe_3O_4-S/PS exhibit higher selectivity of $Fe^{IV}=O^{2+}$ formation than other systems, due to the higher iron dissolution. This suggests a homogeneous PS activation by $Fe^{IV}=O^{2+}$ formed from the dissolved iron ions.

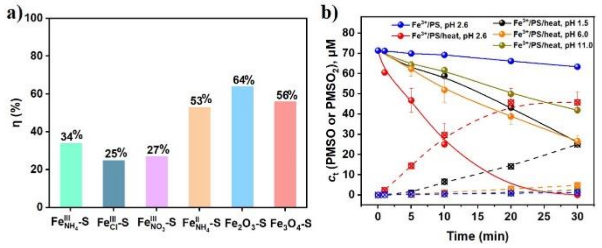

Figure 1. (a) Relative selectivity of $PMSO_2$ production in the selected systems within 15 min; (b) Generation of $PMSO_2$ (dotted line) and loss of PMSO (solid line)

Figure 1b shows the generation of $Fe^{IV}=O^{2+}$ relys on $SO_4^{\bullet-}$ yield and hydrolyzed intermediates of Fe^{3+} (under dufferent pH), which is a single-electron transfer process more readily driven by $SO_4^{\bullet-}$ to oxidize $Fe(OH)(H_2O)_5^{2+}$ intermediate to form $Fe^{IV}=O^{2+}$ at pH < 6.0.

2.4. *Investigation of PS activation mechanism*

In order to determine whether the FeS-driven PS activation is stoichiometric or catalytic, PS consumption was monitored during several activation cycles in the presence of ethanol, which acts as a scavenger of radicals. In the systems $Fe^{II}_{NH_4}$-S/PS, Fe_2O_3-S/PS, and Fe_3O_4-S/PS, about 20 times the stoichiometric amount of PS was activated relative to the FeS_x, and about 70-fold more in the $Fe^{III}_{NH_4}$-S-S/PS, Fe^{III}_{Cl} -S/PS and $Fe^{III}_{NO_3}$-S/PS systems (as in Figure 2). This is significantly higher than the theoretical activation of PS by FeS and FeS_2 by electron transfer. This emphasizes the existence of homolytic catalytic activation of PS by the iron sulfides produced. Among these reaction systems, $Fe^{III}_{NH_4}$-S-S, Fe^{III}_{Cl} -S and $Fe^{III}_{NO_3}$-S exhibit higher PS activation capability. This demonstrates that pyrite and troilite crystal phases are stable for longer-term PS activation through a homolytic cleavage.

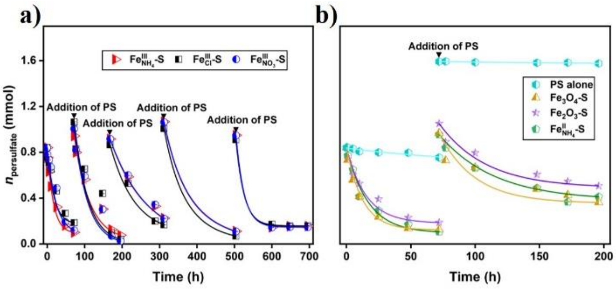

Figure 2 Long-term PS activation.

3. Conclusion

This study highlights the structure-activity relationship of differently prepared iron sulfide minerals in PS activation. Of the minerals tested, pyrite demonstrated superior catalytic activity and stability, effectively activating PS through surface-mediated homolytic cleavage. Kinetic isotope effect experiments confirmed that pyrite and mackinawite both facilitate the generation of $SO_4^{\bullet-}$, with subsequent formation of $Fe^{IV}=O^{2+}$ via single-electron transfer involving $Fe(OH)(H_2O)^{2+}$ intermediates. These findings offer insights for designing efficient iron sulfide-based catalysts for pollutant degradation.

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