



Research paper

Insights into perovskite-catalyzed peroxymonosulfate activation: Maneuverable cobalt sites for promoted evolution of sulfate radicals



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ABSTRACT

Metal-based catalysis has significantly contributed to the chemical community especially in environmental science. However, the knowledge of cobalt-based perovskite for aqueous phase oxidation still remains equivocal and insufficient. In this study, we discovered that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) perovskite was exclusively effective for peroxymonosulfate (PMS) activation to produce free radicals, whereas the BSCF was inert to activate peroxydisulfate (PDS) and hydrogen peroxide. The BSCF/PMS exhibited superior performance to the benchmark Co_3O_4 nanocrystals and other classical PMS activators such as $\alpha\text{-MnO}_2$ and spinel CoFe_2O_4 , meanwhile achieving an impressive stability with manipulated cobalt leaching in neutral and basic environment. *In situ* electron paramagnetic resonance (EPR) revealed the evolution of massive sulfate radicals ($\text{SO}_4\cdot^-$) and hydroxyl radicals ($\cdot\text{OH}$) during the oxidation. A comprehensively comparative study of BSCF and Co_3O_4 nanocrystals was performed, including electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) in PMS solution as well as hydrogen temperature-programmed reduction (H_2 -TPR) and oxygen temperature-programmed desorption (O_2 -TPD) tests. The results unveil that the cobalt-based perovskite, BSCF, exhibited a better electrical conductivity and redox potential than the spinel cobalt oxide to interact with PMS. More importantly, the oxygen vacancies and less-electronegativity A-site metals may secure cobalt sites with a lower valence state for donating electrons to PMS simultaneously for radical generation. This study advances the mechanism of cobalt-based heterogeneous catalysis in environmental remediation.

1. Introduction

Sulfate radical ($\text{SO}_4\cdot^-$) based advanced oxidation processes (SR-AOPs) have aroused immense interests in environmental remediation in recent years. Sulfate radicals produced from persulfates exhibit several merits to hydroxyl radicals ($\cdot\text{OH}$) from Fenton reactions, such as a higher oxidative capability (1.8–2.7 V NHE vs 2.5 V NHE of $\cdot\text{OH}$), a longer half-life period (30–40 μs vs 20 ns of $\cdot\text{OH}$), a better selectivity to target organics in complicated environment, and greater adaptive capability to a wide pH range from 2 to 8 (vs ~ 3.0 of Fenton reactions) [1–3]. Among persulfate salts, peroxymonosulfate (PMS) with an asymmetric structure ($\text{HO}-\text{O}-\text{SO}_3^-$) and a longer superoxide $\text{O}-\text{O}$ bond ($l_{\text{O}-\text{O}} = 1.326 \text{ \AA}$) is believed more easily to be dissociated by a catalyst to generate $\text{SO}_4\cdot^-$ than peroxydisulfate (PDS), which possesses a symmetric structure (${}^{-3}\text{OS}-\text{O}-\text{O}-\text{SO}_3^-$) and a more compact $\text{O}-\text{O}$ bond ($l_{\text{O}-\text{O}} = 1.322 \text{ \AA}$) [4,5].

Dionysiou and co-workers investigated a series of transition metals for generation of inorganic radicals from PMS and discovered that cobalt ions (Co^{2+}) were the most effective homogeneous catalysts for PMS activation [6,7]. Supported cobalt oxides on various other metal-oxide or carbon substrates were also developed as effective heterogeneous catalysts to minimize the toxic cobalt leaching and promote the dispersion of the cobalt oxide crystals [8–11]. Cobalt-containing spinel oxides such as CoFe_2O_4 and CuCo_2O_4 were also demonstrated to present a great activity for PMS activation owing to a synergistic effect of the redox couples between the different metal components [12–14]. More recently, Pang et al. applied LaCoO_3 perovskite to generate sulfate radicals from PMS for rapid mineralization of aqueous contaminants [15]. The La-based perovskites (LaMO_3 , M = Co, Cu, Fe, and Ni) were further investigated and LaCoO_3 exhibited the best performance, confirming the critical role of cobalt in PMS activation [16].

In the heterogeneous cobalt-based catalysis, the catalytic activity of

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cobalt can be manipulated via several protocols. Firstly, the catalytic activity of cobalt oxide is intimately related with the surficial atom arrangement that governs the activation energy, kinetic behaviors, and electron-transport processes in binding with reactants and breaking the chemical bond in a catalytic reaction [17–20]. Thus, shape-controlled spinel Co_3O_4 could be synthesized by nano-engineering to predominantly expose certain crystal planes, which has been demonstrated as facet-dependent activity in methane combustion and carbon monoxide (CO) oxidation [21]. It is supposed that the [001] and [111] planes are mainly composed of Co^{2+} , which might present a better activity than other planes for PMS activation due to lower reductive potential of cobalt as an electron-donor. Secondly, supporting substrates would not only promote the dispersion of cobalt oxide with small particle sizes and high surface areas herein providing more active centers, but also impressively modulate the surface chemistry of the cobalt oxides via the covalent bonds between the catalysts and supports [22,23]. Studies have shown that the supports such as graphene [24], activated carbon fiber [25], and silicon oxide [26] could effectively enhance the activity of cobalt oxide for PMS activation. Moreover, substitutional doping other 3d-transition-metal cations into the tetrahedral site ($\text{Co}_{\text{Td}}^{2+}$) and octahedral site ($\text{Co}_{\text{Oh}}^{3+}$) of Co_3O_4 and rational design of mixed-metal spinel oxides such as $\text{Co}_{3-x}\text{M}_x\text{O}_4$ ($1 \leq x \leq 2$, $\text{M} = \text{Zn}, \text{Ni}, \text{Fe}, \text{Mn}$) could further enhance the activity of cobalt, because the formation of Co–O–M bond could optimize the spinel structure and modulate the spin culture and electron localization of cobalt [27–29]. Meanwhile, the charge transfer from the redox couples between $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{M}^{n+}/\text{M}^{(n+1)+}$ in the mixed metal oxides may further promote the catalytic activity for PMS activation as mentioned above.

Distinct from the mixed metal spinel oxides that could only be composed of several limited transition metal oxides to form a stable spinel structure, the perovskite oxides with a typical ABO_3 structure, where A sites are larger-sized alkali and rare earth metals and B sites are 3d transition metal ions, are capable of hosting more than 90% of metal elements in the periodic table [30,31]. More importantly, the structural, physicochemical and electronic properties of perovskites could be easily tuned by regulating the category and proportion of chemical compositions, providing a versatile substrate in the community of chemistry and materials science. Herein, the perovskites have attained great successes in a marriage of diverse catalytic progresses stretching from electrocatalysis to photocatalysis [32,33]. Nevertheless, several recent studies employed cobalt-based perovskites as persulfate activators to generate sulfate radicals, while the massive metal-leaching severely plagued these materials as environmentally-benign catalysts for green remediation due to the strong toxicity of cobalt [15,16,34,35]. Additionally, the mechanism of perovskite-catalyzed peroxy-monosulfate still remains piecemeal and ambiguous, which requires an insightful study for the identification of the inherent active sites and unravelling the evolution of the reactive radicals. In this study, we utilized $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3.8}$ (BSCF) perovskite as a model catalyst for mediating sulfate radicals by activating PMS. Various *in situ* characterizations and comprehensive comparison with the benchmark nanocrystals of cobalt oxide were conducted. The BSCF demonstrated greater electrical conductivity and redox potential than cobalt oxide nanocrystals to bond with PMS for charge transport, benefited from the surficial oxygen vacancies and less electronegative A-site metals. Meanwhile, the initially produced hydroxyl radicals were witnessed to play a crucial role for mediating sulfate radicals, which were further confirmed as the dominating reactive species. We dedicate this study to unveiling the evolution of free radicals from PMS with the perovskite and to probing the manipulated cobalt sites in mixed metal oxides for the heterogeneous catalysis.

2. Materials and methods

2.1. Chemicals and materials preparation

All the chemicals were purchased from Sigma-Aldrich, Australia and received without further purification. The perovskite oxides such as BSCF, $\text{SrCo}_{0.9}\text{Ti}_{0.1}\text{O}_{3.8}$ (SCT), $\text{PrBaCo}_2\text{O}_{5.8}$ (PBC) and LaCoO_3 were prepared via a classic sol–gel approach and calcination reported in our previous study [36]. In a typical process (e.g. BSCF), a stoichiometric dosage of metal nitrates such as $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a molar ratio of 5:5:8:2 was first dissolved in deionized water to form a homogeneous solution at 100 °C. Ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) were then introduced into the mixture solution at a molar ratio of 1:2:1 (EDTA:C:A:total metal ions). The pH value of the solution was adjusted to around 6 with ammonium solution and heated at 100 °C to evaporate water and produce a transparent gel. The gel was pre-treated at 250 °C for 5 h and then calcined at 950 °C for 5 h in static air to be transformed into a uniformly mixed metal oxide with a characteristic perovskite crystal. SCT, PBC, and LaCoO_3 were obtained at 1000, 1000, and 800 °C, accordingly. The resulting products were ground finely for future use. The detailed preparation and structural information (Fig. S1) of other metal oxides such as cobalt oxide, manganese oxides, and spinel CoFe_2O_4 can be found in the Supplementary Data.

2.2. Characterization of perovskite

The morphologies of BSCF perovskite and spinel Co_3O_4 were revealed by a FESEM (Zeiss Neon 40EsB FIBSEM) in Fig. S2. The crystallographic structure of metal-based catalysts was determined by powder X-ray diffraction (XRD) on a Bruker D8A instrument. The XRD spectra were recorded with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.78897 \text{ nm}$) within a two-theta range of 10–80° at a scanning speed of 2° min^{-1} . The specific surface areas (SSAs) and pore structure were acquired from a Micrometrics TriStar II equipment at -196°C estimated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) equations, respectively. The redox potential of perovskite was evaluated by oxygen temperature-programmed desorption (O_2 -TPD) and hydrogen temperature-programmed reduction (H_2 -TPR). The O_2 -TPD was performed from room temperature to 1000 °C under a constant argon flow. Oxygen was detected by an on-line mass spectrometer. The H_2 -TPR was recorded on a ChemBET 3000 equipment. The sample was treated at 400 °C for 2 h under flowing N_2 to clean the surface contaminants and then reduced by 5% H_2 in N_2 at a flow rate of 90 mL min^{-1} and a ramping temperature of $5^\circ \text{C min}^{-1}$ from 35 to 1000 °C. The concentration of metal ions in the reaction solution was detected on a Perkin Optima 8300 ICP-OES. The surface elemental analysis was performed on an X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe) with an $\text{Al-K}\alpha$ X-ray gun. The XPS spectra were analyzed with CasaXPS software using a Shirley background, and Voigt functions with a 30% Lorentzian component were applied for the component deconvolutions.

2.3. Catalytic evaluation of catalysts

The catalytic performance of the perovskites was evaluated for peroxy-monosulfate activation and organic oxidation. The experiments were carried out in a batch reactor in a water bath maintained at 25 °C. The fixed amounts of PMS and catalyst were simultaneously introduced into the organic solution to initialize the oxidation; meanwhile mechanical stirring was kept to ensure a homogeneous solution throughout the reaction. Periodically, the mixture was withdrawn by a syringe and filtered via a $0.45 \mu\text{m}$ membrane, and the filtrate was mixed with methanol ($V_{\text{filtration}}:V_{\text{methanol}} = 2:1$) to quench the reactive radicals and terminate the oxidation. The sample was then analyzed on a high-performance liquid chromatography (HPLC, Thermo-Fisher) using

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