



Surface-loaded metal nanoparticles for peroxymonosulfate activation: Efficiency and mechanism reconnaissance

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ABSTRACT

This study comparatively examines the efficiency and mechanism of peroxymonosulfate (PMS) activation by twenty metal and metalloid nanoparticles loaded on alumina. Among the tested metals, Co exhibited the highest capacity for PMS activation and accompanying oxidative degradation of trichlorophenol (TCP), a representative organic pollutant in water. Other transition metals such as Mn, Cu, Mo, Ni, and W exhibited moderate activity, while Ti, Zn, Fe, V, Cr, Al, and Si were mostly ineffective. In contrast, all of the tested noble metals (Ru, Rh, Pd, Ir, Pt, and Au) except Ag enabled rapid PMS activation and TCP degradation, outperforming Co at acidic pH. Transition metals with noticeable PMS activation capacity differed from noble metals in several aspects, such as the effect of radical quenching on 4-chlorophenol (4-CP) degradation, electron paramagnetic resonance spectral features, oxidative conversion of bromide into bromate, and oxidation intermediate distribution. They were also distinguishable with respect to the dependence of PMS degradation on the presence of an electron donor (i.e., TCP), the capacity to activate peroxydisulfate (PDS), and the electrochemical response upon addition of PMS and 4-CP when fabricated into electrodes. Based on these observations, we categorized surface-loaded metal nanoparticles into two groups with distinctive PMS activation mechanisms: (i) transition metals such as Co, Cu, and Mo that activate PMS to produce highly reactive sulfate radicals ($\text{SO}_4^{\cdot-}$); and (ii) noble metals such as Rh, Ir, and Au that mediated direct electron transfer from organic compound (electron donor) to persulfate (electron acceptor) without involving the formation of radical species.

1. Introduction

Advanced oxidation processes (AOPs) for water treatment utilize highly reactive but short-lived oxidants such as sulfate ($\text{SO}_4^{\cdot-}$) and hydroxyl radicals ($\cdot\text{OH}$) to oxidatively degrade organic pollutants [1,2]. These radicals are generated on-site by the activation of more stable, peroxide-containing precursor chemicals such as persulfate, peracetate, and hydrogen peroxide. Homolytic or heterolytic peroxide bond cleavage is typically achieved by ‘activation’ strategies such as photolysis [3], thermolysis [4], and chemical reduction [5]. Compared to H_2O_2 , a benchmark precursor for AOP, persulfates such as peroxymonosulfate (PMS) and peroxydisulfate (PDS) allow for broader activation strategies because the peroxide bond in persulfate has a higher electron affinity and exhibits a lower bond dissociation energy (e.g., 92 kJ mol⁻¹ for PDS

versus 213 kJ mol⁻¹ for H_2O_2) [6]. For example, thermolysis [4] or reduction by inorganic ions [7] and carbonaceous materials [8,9] can activate persulfate while H_2O_2 cannot. In addition, a wider range of metal-based reagents are known to activate persulfate [10–16], in contrast to H_2O_2 , which can only be activated by a limited number of transition metals such as iron and copper [11].

Metals in their reduced ionic form in water (e.g., Co^{2+}) have been found to readily activate persulfate, leading to the formation of $\text{SO}_4^{\cdot-}$ and subsequent degradation of organic pollutants [11]. Heterogeneous catalysts such as zero valent metals (e.g., Fe nanoparticles) [17,18], metal oxides (e.g., CuO [16], Mn_2O_3 [15], MnO [14]), and metal oxide composites (e.g., $\text{Co}_3\text{O}_4/\text{MnO}_2$ [13], CuFe_2O_4 [12], CoFe_2O_4 [19], $\text{Co}_3\text{O}_4/\text{graphene oxide}$ [20]) have also been found to initiate rapid persulfate activation. Among the various material architectures

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explored to date, noble metal clusters loaded onto metal oxide substrates (e.g., Pt/Al₂O₃, Au/TiO₂) have been demonstrated to exhibit the highest persulfate activation capacity over a wide pH range [10]. Despite the general recognition that the electron-donating potential of metals readily achieves one-electron reduction reaction instrumental in the production of SO₄^{•-} from persulfate, the attempts to screen metal-based activator candidates have been made with a relatively small set of metals (e.g., Co, Fe, Cu, and Mn) [11–14,17,21]. It is noteworthy that the choice of Co²⁺ as a benchmark PMS activator was also made based on the comparison in PMS activation performance among select metal ions (i.e., Co²⁺, Ru²⁺, Fe²⁺, Ni²⁺, and Ag⁺) rather than the comprehensive evaluation of a broad range of metals [11].

There has been a controversy regarding the mechanism underlying persulfate activation. Some studies have indicated the involvement of SO₄^{•-} and [•]OH in the oxidation of organic compounds and others provide a compelling line of evidence for an alternative non-radical reaction pathway, i.e., direct electron transfer from organic pollutants to persulfate utilizing the catalysts as an electron-transfer mediator. The alternative reaction pathway involving no radical attack took place mostly when carbonaceous materials such as carbon nanotubes (CNTs) [5,9,22] and graphited nanodiamonds [23] were applied as persulfate activators. Surface modification of nanocarbon activators was suggested to switch the main reaction pathway for persulfate activation [24,25]. Positively charged carbons resulting from N-doping of CNTs formed the reactive PMS complexes, which promoted the electron exchange between organics and PMS molecules involved in surface complexation as the non-radical degradative route. Multiple outer carbon shells observed on the nanodiamonds annealed at the extremely high temperatures (~1100 °C) caused preferential PMS adsorption followed by surface complexation, facilitating PMS activation not reliant on radicals. On the other hand, few reports demonstrated that select metal-based activators such as CuO [16] and noble metals [10] could initiate the non-radical persulfate activation, which was explicitly distinguished from that induced by Co²⁺ based on (i) quenching effect of methanol, (ii) EPR (electron paramagnetic resonance) spectral features, (iii) substrate-specificity, and (iv) intermediate distribution. The previous findings likely reveal the possibility that persulfate activation mechanism may vary depending on the choice of metal.

A growing interest in utilizing the strong oxidation potential of SO₄^{•-} ($E^{\circ}(\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}) = 2.5\text{--}3.1 \text{ V}_{\text{NHE}}$) [26] produced from persulfate activation and the promise of being able to employ metals as heterogeneous activators have motivated a search for optimal metals and an ideal composite structure. In this respect, metal nanoparticles loaded onto substrates are of particular interest because of their superior persulfate activation and organic pollutant degradation kinetics, as demonstrated previously with selected metals [10,27]. However, there is still a dearth of information as to the optimal metal species for this application and the prevalent mechanism of persulfate activation and pollutant degradation, especially with respect to the involvement of radical species. In this study, we performed a comprehensive screening of 20 metals (14 transition metals, 6 noble metals, 2 other metallic/semi-metallic elements that have been used for similar catalytic processes including persulfate activation) and evaluated their performance for persulfate activation and oxidation of selected organic pollutants. The same material architecture (i.e., nanosized metal particles immobilized on Al₂O₃ using arc plasma deposition technique; referred as to M/Al₂O₃) was used to study the intrinsic property of the metals exclusively.

2. Materials and methods

2.1. Reagents

All chemicals were of reagent grade and used as-received, including aluminum oxide (Al₂O₃, Puralox TH 100/150, Sasol; BET surface area = 150 m²/g; average particle size = 35 μm), potassium monopersulfate (Oxone®, Sigma-Aldrich), potassium peroxydisulfate (Sigma-

Aldrich), 4-chlorophenol (4-CP; Aldrich), 2,4,6-trichlorophenol (TCP; Aldrich), 5-*tert*-butoxycarbonyl-5-methyl-1-pyrroline-*N*-oxide (BMPO) (ENZO Life Sciences, Inc.), methanol (J.T. Baker), potassium iodide (Sigma-Aldrich), sodium bromide (Aldrich), sodium bromate (Sigma-Aldrich), sodium chloride (Sigma-Aldrich), sodium carbonate (Sigma-Aldrich), sodium bicarbonate (Sigma-Aldrich), sodium sulfate (Sigma-Aldrich), sodium phosphate monobasic (Sigma-Aldrich), sodium phosphate dibasic (Sigma-Aldrich), phosphoric acid (Aldrich), and acetonitrile (J.T. Baker). Ultrapure water (> 18 MΩ·cm) produced by a Milli-Q Water Purification System (Millipore) was used for the preparation of all experimental solutions and suspensions.

2.2. Preparation of surface-loaded metal nanoparticles

Metals were loaded as nano-sized particles on the surface of Al₂O₃ substrate using a coaxial pulsed arc-plasma deposition (APD) system (ULVAC, ARL-300) (Figure S1 is a schematic of the APD process) [28]. A columnar cathode (comprising the material to be deposited) was located at the center of a reaction chamber. A trigger electrode was placed at the outer rim of the cathode and a cylindrical anode was coaxially aligned with the cathode. Al₂O₃ powders were placed at the bottom of the chamber, directed toward the plasma source, and mechanically stirred for uniform dispersion. An electric charge was accumulated in a discharge condenser (capacity = 1080 μF; connected to the cathode) at a discharge voltage of 200 V A highly ionized metal plasma was then instantly generated by a trigger pulse on the cathode at room temperature under vacuum (10⁻⁵ Torr), which led to the dispersion of metal nanoparticles on the Al₂O₃ surface. The pre-determined repeated plasma shots (10,000) from various metal sources were irradiated onto Al₂O₃ for the preparation of M/Al₂O₃ with the same metal loading (ca. 1.0 wt%).

Energy dispersive spectroscopic (EDS) analysis of select samples (i.e., the M/Al₂O₃ samples that showed noticeable persulfate activation capability as discussed below) suggested that the production of ionized metal plasma led to the successful deposition of metals on alumina surface (Figures S2). The transmission electron microscopic images showed that metal particles were uniformly surface-loaded with an average diameter of ca. 2–5 nm (Figures S3). The oxidation states of the M/Al₂O₃ samples were identified with X-ray photoelectron spectroscopy (XPS, ULVAC-PHI X-TOOL) using the Al Kα line (1486.7 eV) as an excitation source. The spectra of metal-deposited Al₂O₃ showed that most metals were coated as their corresponding oxides, with the exception of Pt and Au, which were present in metallic forms (Figures S4a–r). In particular, the spectral features of Pd/Al₂O₃ and Rh/Al₂O₃ implied the co-presence of metallic and oxidized forms (e.g., a binary mixture of Pd⁰ and PdO) (Figures S4h and S4o). Despite these variations, we have used the same nomenclature i.e., M/Al₂O₃ or simply M, and not MO_x/Al₂O₃ or MO_x.

In order to explore the possibility that the oxidation state of supported metal could affect persulfate activation performance and mechanism, we selected surface-loaded metals that caused significant organic oxidation associated with PMS activation (e.g., Co, Mn, Ir, and Pd) and thermally treated them at 700 °C for 2 h under a flowing hydrogen atmosphere. The peak shift in the XPS spectra (except Co) confirmed the further reduction of metals immobilized on alumina to the corresponding metallic phases (Figure S5).

2.3. Experimental procedure and analytical methods

Oxidative degradation of select organic pollutants proceeded in a magnetically stirred 40 mL reactor under air-equilibrated conditions. Typical experimental suspensions contained 0.25 g/L of M/Al₂O₃, 1 mM persulfate, and 0.1 mM target substrate. The aqueous suspensions were unbuffered when the experiments were performed at acidic pH, and buffered using 2 mM bicarbonate buffer in order to evaluate the persulfate-activating capacity of M/Al₂O₃ at pH 7. Sample aliquots were

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