Chemical Engineering Science 160 (2017) 96–105

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

LaMO$_3$ perovskites (M=Co, Cu, Fe and Ni) as heterogeneous catalysts for activating peroxymonosulfate in water

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ARTICLE INFO

Keywords:
Perovskites
Lanthanum
Peroxymonosulfate
Rhodamine B

ABSTRACT

Although perovskites are extensively investigated in many areas, studies using perovskites as catalysts to activate oxidants for chemical oxidations are still quite limited. While various transition metals can be inserted into perovskites to form different perovskites, it is critical to investigate the effects of various transition metallic substituents on the activation of oxidants in chemical oxidation reactions. In this study, we propose to evaluate various metallic substituents in Lanthanum (La)-based perovskites (LaMO$_3$ (M: Co, Cu, Fe and Ni)) for activating a strong oxidant, peroxymonosulfate (POMS), in order to degrade organic contaminants. Rhodamine B (RB) decolorization is used as a model test to evaluate generation of sulfate radicals from activation of POMS by LaMO$_3$. LaCoO$_3$ was found to exhibit the highest catalytic activity, followed by LaNiO$_3$, LaCuO$_3$ and then LaFeO$_3$. LaCoO$_3$ was then selected as a representative LaMO$_3$ to be further investigated for the behavior of POMS activation under various conditions. LaCoO$_3$-activated POMS was favorable under neutral conditions and at high temperatures, but less effective in the presence of NaCl. The mechanism of RB decolorization by LaCoO$_3$-activated POMS was elucidated by examining the effects of radical inhibitors and attributed primarily to sulfate radicals and hydroxyl radicals to a lesser extent. We also found that both La^{3+} and Co^{3+}/Co^{2+} ions contribute to catalytic decomposition of POMS for yielding sulfate radicals. LaCoO$_3$ was also shown to activate POMS for RB decolorization over multiple trials without losing efficiency. These results reveal that LaCoO$_3$ is a recyclable and effective La-based perovskite for POMS activation, which can be used for degradation of organic contaminants.

1. Introduction

Chemical oxidation is a useful technique for treatment of organic contaminants (Oturan and Aaron, 2014; Ikehata et al., 2006; Klavarioti et al., 2009) as well as organic synthesis (Hoelderich and Kollmer, 2000). Chemical oxidation generally involves highly oxidizing radicals, for instance hydroxyl ($OH^{\bullet}$) and sulfate ($SO_4^{\bullet -}$) radicals. To obtain these radicals, strong oxidants (*e.g.*, hydrogen peroxide (H_2O_2), persulfate and peroxymonosulfate (POMS)) are usually adopted as sources which require proper activating processes. To date, processes for activating H_2O_2 have been intensely developed and used in various areas, including environmental remediation (Liao et al., 2009), synthesis of chemicals (Noyori et al., 2003), healthcare (Li and Greenwall, 2013), *etc.* Processes for activating persulfate and POMS also recently received much attention because $SO_4^{\bullet -}$ can exhibit a similar or even higher oxidation power than $OH^{\bullet}$ (Neta et al., 1988). Sulfate radicals have also been reported to show relatively high selectivity in attacking aromatic/unsaturated chemical structures (Neta et al., 1988; Antoniou et al., 2010) with a much longer half-life than $OH^{\bullet}$ (Olmez-Hanci and Arslan-Alaton, 2013; Janzen et al., 1992).

While activation of persulfate has been thoroughly studied, activation of POMS is also promising because POMS is an environmentally-friendly and easily-accessible reagent (Hu and Long, 2016). Several approaches have been proposed to activate POMS, such as ultrasound (Li et al., 2013; Kurukutla et al., 2014), light irradiation (Yang et al., 2010; Gao et al., 2012), thermal treatments (Yang et al., 2010; Huang et al., 2002) as well as catalysts (Anipsitakis et al., 2005; Wei et al., 2015; Lin et al., 2015a, 2015b). Among these approaches, activation of POMS by catalysts is considered relatively practical (Yang et al., 2009) because the other aforementioned processes demand continuous energy input. Thus, a number of metals and metal oxides have been studied and shown to activate POMS, including iron, cobalt and copper (Lin et al., 2015a, 2015c; Lin and Chen, 2016; Oh et al., 2016, 2014, 2015; Andrew Lin and Zhang, 2016). A number of metallic catalysts

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http://dx.doi.org/10.1016/j.ces.2016.11.017
Received 25 July 2016; Received in revised form 11 October 2016; Accepted 6 November 2016

have been proposed to activate POMS (*e.g.*, cobalt, copper, iron and manganese) (Lin et al., 2015a, 2015c; Lin and Chen, 2016; Oh et al., 2016, 2014, 2015; Andrew Lin and Zhang, 2016). Nevertheless, addition of homogeneous transition metal ions to activate POMS leads to secondary pollution (Guo et al., 2015; Do et al., 2009; Wacławek et al., 2015; Chan and Chu, 2009). Thus, heterogeneous metallic nanoparticles have also been developed for activation of POMS (Anipsitakis et al., 2005; Chen et al., 2008); however, these metallic nanoparticles are prone to aggregation, diminishing their catalytic activities (Anipsitakis et al., 2005; Chen et al., 2008; Guo et al., 2013). To this end, many studies propose immobilizing metallic nanoparticles onto supports to prevent release of nanoparticles to the environment (Yang et al., 2007). Various supports have been evaluated to prepare supported metallic catalysts, including SiO_2 (Yang et al., 2008), TiO_2 (Zhu et al., 2013; Du et al., 2016), Al_2O_3 (Yang et al., 2008), MnO_2 (Liang et al., 2012), fly ash (Muhammad et al., 2012) and carbonaceous materials (Lin et al., 2015b; Xu et al., 2015a, 2015b; Yao et al., 2012; Wang et al., 2016; Shi et al., 2013; Zhou et al., 2015). However, synthesis of these supported metallic catalysts typically involves complex procedures and multiple reagents, leading to relatively long preparation time. Thus, it remains necessary to develop other metal/metal oxide materials to expand the spectrum of heterogeneous catalysts for activating POMS.

Recently, perovskite-type metal oxides are increasingly investigated in various areas, including solar energy (Petrović et al., 2015), electrochemistry (Weidenkaff, 2004), sensors (Ghasdi and Alamdari, 2010) and catalysis (Zhu et al., 2014). In particular, perovskites are considered as promising heterogeneous catalysts (Zhu et al., 2014) because perovskite-type metal oxides exhibit high stability under aggressive conditions and a relatively high degree of stabilization of transition metals in their oxidation states, as well as oxygen mobility within perovskites (Taran et al., 2016). These characteristics make perovskites promising catalysts for chemical oxidation (Taran et al., 2016). As perovskites can consist of various transition metals, it is critical to investigate the effects of various transition metals inserted into perovskites on activating oxidants. Thus, Taran et al. recently evaluated effects of various transition metals in Lanthanum (La)-based perovskites, the most common type of perovskite (Ghasdi and Alamdari, 2010; Taran et al., 2016; Villoria et al., 2011), for activating H_2O_2 to degrade phenol in water (Taran et al., 2016). Nevertheless, as studies of activation of POMS by perovskites are still limited (Chi et al., 2015), to our best knowledge, almost no studies have been conducted to investigate effects of various transition metallic substituents of perovskites on activation of POMS. Herein, we propose to evaluate various $LaMO_3$ perovskites for POMS activation.

In this study, various $LaMO_3$ (*i.e.*, $LaCoO_3$, $LaCuO_3$, $LaFeO_3$ and $LaNiO_3$) are prepared and used to evaluate catalytic activities of $LaMO_3$ for activating POMS. Decolorization of Rhodamine B (RB) by $SO_4^{\bullet-}$ from activation of POMS is adopted as a model test because RB is a toxic dye and extensively employed to evaluate POMS activation by various catalysts, such as Fe^{2+} (Kurukutla et al., 2014), $BiVO_4$ (Liu et al., 2016b), CoFe/SBA-15 (Hu et al., 2015), $Co_xMn_{3-x}O_4$ (Yao et al., 2015), Cu/ZSM5 (Ji et al., 2014), magnetic carbon-supported metals (Lin et al., 2015a, 2016a, 2016b; Lin and Chen, 2017; Andrew Lin and Hsu, 2015), carbon nitride (Lin and Chen, 2016; Tao et al., 2015; Lin and Zhang, 2017), α-MnO_2 (Liu et al., 2016a), metal organic frameworks (Lin et al., 2016c; Lin and Chang, 2015), and α-sulfur (Andrew Lin and Zhang, 2016). RB decolorization by various $LaMO_3$-activated POMS was compared and corresponding activation energies were calculated. Various effects, including $LaMO_3$ and POMS concentrations, temperature, pH, and salt, on RB decolorization were examined. Mechanisms of RB decolorization by $LaMO_3$-activated POMS and activation of POMS by $LaMO_3$ were revealed and proposed. Recyclability of $LaMO_3$ was tested to examine whether $LaMO_3$ perovskites can be re-used.

2. Experimental

2.1. Preparation and characterization of $LaMO_3$ perovskites

All reagents involved in this study are commercially available and used directly without purification. $LaMO_3$ perovskites were prepared according to reported glycine combustion methods (Taran et al., 2016; Wang et al., 2006). In brief, 20 mmol of $La(NO_3)_3$ and a metal nitrate (*e.g.*, Co, Cu, Fe and Ni) as well as 80 mmol of glycine were added to 100 mL of deionized (DI) water. The mixture was stirred and maintained at 60 °C for 12 h to yield a sol-like solution, which was subsequently evaporated to remove water and then calcined at 700 °C for 2 h in air to obtain $LaMO_3$ perovskite.

The as-prepared perovskites were characterized for morphologies using scanning electronic microscopies (SEM) (JEOL JSM-6700, Japan) equipped with Energy-dispersive X-ray spectroscopy (EDS) (Oxford Instrument, UK). Crystalline structures of perovskites were determined by an X-ray diffractometer (Bruker D8 Discover, USA) with copper as an anode (40 mA, 35 kV). Surface areas of perovskites were measured by a gas sorption analyzer (Quantachrome AutoSorb IQ, USA).

2.2. Activation of POMS by $LaMO_3$ perovskites

Catalytic activation of POMS by perovskites was evaluated *via* decolorization of RB dye. In a typical decolorization experiment, 20 mg of POMS powder was added to 200 mL of RB solution with a starting concentration (C_0) of 10 mg L^{-1}, followed by addition of 20 mg of perovskite. The mixture was stirred at 300 rpm and maintained at a fixed temperature. Sample aliquots were withdrawn from the RB solution and the remaining concentration at a pre-set time, t (C_t) was measured by a UV–Vis spectrophotometer (ChromTech 2200, Taiwan). Initial pH of RB solution was changed to 3, 5, 7, 9, and 11 using HNO_3 or NaOH to examine the effect of pH.

Effects of co-existing compounds were also studied by adding NaCl and radical inhibitors. Ascorbic acid, *tert*-butyl alcohol (TBA) and methanol were adopted as radical inhibitors to provide insights in the decolorization mechanism using activation of POMS by perovskites. Ascorbic acid was selected because it is a universal radical scavenger (Niki, 1991). The inhibition on RB decolorization by ascorbic acid indicates whether RB decolorization could be attributed to high-oxidation-potential radicals. Moreover, it was necessary to determine which types of radicals appeared during POMS activation to contribute to RB decolorization. To this end, tert-butyl alcohol (TBA), which does not consist of α-hydrogen, was employed as an indicator for $OH^{\bullet}$ because TBA rapidly reacts with $OH^{\bullet}$ (rate constant=7.6×10^8 M^{-1} s^{-1}), while the rate constant for the reaction of TBA with $SO_4^{\bullet-}$ is considerably lower (*i.e.*, 4×10^5 M^{-1} s^{-1}). On the other hand, methanol, consisting of α-hydrogen, is able to quickly react with both $OH^{\bullet}$ and $SO_4^{\bullet-}$ (rate constant=9.7×10^8 M^{-1} s^{-1} for $OH^{\bullet}$ and 3.2×10^6 M^{-1} s^{-1} for $SO_4^{\bullet-}$). Therefore, methanol was employed as an indicator for both $OH^{\bullet}$ and $SO_4^{\bullet-}$ (Huang et al., 2014).

In the experiment for investigating the effect of inhibitors, a certain initial concentration of inhibitor (*i.e.*, 0.1 M) was added to a RB solution. Subsequently, POMS and $LaMO_3$ were added to the RB solution to start the decolorization experiment. During the decolorization, we only monitored variation of RB concentration instead of the concentration of inhibitors to determine whether RB decolorization was inhibited. Recyclability of perovskites for activating POMS was tested by using recycled perovskites for decolorization over multiple cycles.