



LaFeO₃ and BiFeO₃ perovskites as nanocatalysts for contaminant degradation in heterogeneous Fenton-like reactions



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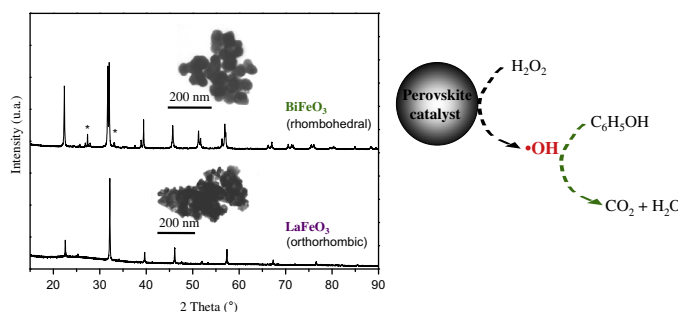
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HIGHLIGHTS

- LaFeO₃ and BiFeO₃ prepared and tested as catalysts for heterogeneous Fenton reaction.
- Nano-crystalline perovskites obtained by implementation of sol-gel method.
- LaFeO₃ and BiFeO₃ showed high catalytic activity in phenol oxidation at pH 7.
- Excellent stability of BiFeO₃ in four re-use cycles.
- Mechanistic studies based on isotope fractionation experiments indicate dominant role of ·OH.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study examines the applicability of two iron-containing perovskites, LaFeO₃ (LFO) and BiFeO₃ (BFO), as nanocatalysts for heterogeneous Fenton-like reactions using phenol and methyl *tert*-butyl ether (MTBE) as model contaminants. LFO and BFO synthesized according to a sol-gel method using citric acid as complexing agent have a crystallite size of about 60–70 nm with specific surface areas of 5.2 m² g⁻¹ for LFO and 3.2 m² g⁻¹ for BFO. In heterogeneous Fenton-like reactions, LFO and BFO showed similar pseudo-first order rate constants for phenol oxidation ($k'_{LFO} = (0.13 \pm 0.01) \text{ h}^{-1}$ and $k'_{BFO} = (0.15 \pm 0.01) \text{ h}^{-1}$) at pH = 7 when 0.1 g L⁻¹ catalyst and 3.0 g L⁻¹ H₂O₂ were applied. Degradation efficiency was improved for both perovskites by a factor of approximately three when the pH value was slightly decreased to pH = 5. An increase of the reaction temperature from 20 °C to 60 °C during the BFO-catalyzed reaction led to a significant acceleration of phenol removal of about one order of magnitude ($k'_{BFO} = (1.9 \pm 0.1) \text{ h}^{-1}$). High stability and reusability of the BFO particles was confirmed in four successive oxidation batches using MTBE as model contaminant. In addition, the mechanism of the perovskite-catalyzed Fenton-like system was studied by applying compound-specific stable isotope analysis (CSIA). The perovskite-catalyzed oxidation appears to follow a pathway similar to that of the homogeneous Fenton reaction, i.e. ·OH radicals play a dominant role as primary reactive species.

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1. Introduction

Fe²⁺ salts react with hydrogen peroxide (H₂O₂) to generate hydroxyl radicals (·OH) in the homogeneous Fenton reaction [1,2], which has been suggested as an efficient treatment tool for

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degrading recalcitrant pollutants. The main drawbacks of the homogeneous Fenton reaction are: (i) the tight working range of pH (about pH = 3) in order to achieve acceptable reaction rates, and (ii) the production of precipitates, mostly in the form of iron sludge, which requires subsequent removal [1]. In recent years, increasing attention has been paid to research on heterogeneous Fenton-like systems in order to overcome these problems. An optimal solid catalyst for heterogeneous Fenton-like reactions should be able to form $\cdot\text{OH}$ from H_2O_2 over a wide pH range and show high efficiency with respect to contaminant degradation and H_2O_2 utilization, limited metal ion leaching, and long-term stability. Operating costs and environmental compatibility must also be taken into account. Regarding heterogeneous Fenton systems, two main approaches are considered for catalytic activation of H_2O_2 : (i) immobilization of transition metal catalysts on porous materials such as silica, alumina, zeolite, clays or activated carbon [3–5], and (ii) use of non-porous metals or metal oxides [6–8]. Although these types of catalysts were shown to have considerable activities for heterogeneous Fenton-like degradation of various contaminants, there is still room for substantial improvement of the performance with respect to the above-mentioned criteria. Since the catalytic activity of pure iron oxides for Fenton-like oxidation is limited [9], research on the use of mixed metal oxides is receiving increasing interest. Orthoferrites with perovskite structure fabricated as nano-catalysts might be a promising option.

Perovskite-type oxides with the general elemental composition of ABO_3 , where A is a rare earth metal and B a transition metal, have attracted many scientists due to their fascinating and well-defined structure and intrinsic properties. Current applications include solid oxide fuel cells, magnetic and electrode materials, chemical sensors and catalysts [10,11]. The high mobility of oxygen and the stabilization of unusual oxidation states in their structure are believed to govern the catalytic versatility of perovskites [11]. The potential application of perovskites containing transition metals (e.g., A = La and B = Fe, Mn or Cr) as catalyst in carbon-based electrodes has motivated studies elucidating the catalytic H_2O_2 decomposition [12–14]. These studies indicated that H_2O_2 decomposition depends not only on the metal composition but also on the concentration of highly oxidized transition metal sites (e.g., Ni^{III} and Fe^{IV}) [15] and oxygen non-stoichiometry [14].

So far only a few studies have investigated the applicability of perovskite-type oxides in heterogeneous Fenton-like reactions [16–21]. Luo et al. [19] demonstrated interesting catalytic properties of BiFeO_3 nanoparticles for Rhodamine B (RhB) degradation at pH = 5 (e.g. half-life $t_{50} = 20$ min for $c_{\text{cat}} = 0.5 \text{ g L}^{-1}$, $c_{0,\text{RhB}} = 10 \mu\text{M}$ and $c_{0,\text{H}_2\text{O}_2} = 10 \text{ mM}$). For RhB as a large molecule which is negatively charged at pH = 5, electrostatic attraction and thus adsorption to the BiFeO_3 surface (showing a positive charge at this pH) might have positively affected the degradation. In contrast, phenol, as an example for compounds with low adsorption tendency, showed a lower degradation rate than RhB [19].

LaFeO_3 perovskites prepared by the “self-combustion” procedure were studied as heterogeneous Fenton-like catalysts for phenol degradation in the pH range of 2–4.5 [17]. The sample with the lowest crystal domain size revealed the highest catalytic activity for phenol oxidation at pH = 3.7 and 40 °C (e.g., $t_{50} = 15$ min, $c_{\text{cat}} = 1 \text{ g L}^{-1}$, $c_{0,\text{phenol}} = 0.5 \text{ mM}$, H_2O_2 dosage 2 mM h^{-1}) [17]. Obviously, synthesis conditions strongly influenced the structural characteristics as well as the catalytic activity of the LaFeO_3 samples.

Thus, the aim of our study was to evaluate the applicability of perovskite catalysts for degradation of organic contaminants by heterogeneous Fenton-like oxidation. For this purpose LaFeO_3 (LFO) and BiFeO_3 (BFO), as iron-containing perovskite-type oxides with different crystal structures, were synthesized by sol–gel procedures. Among the various wet chemistry methods for synthesis of nano-sized perovskite materials [22] (self-combustion,

co-precipitation and sol–gel methods), sol–gel procedures are considered to be most promising for up-scaled production based on evaluation of energy consumption, controllability and product properties. The LFO and BFO perovskites were tested as nanocatalysts for heterogeneous Fenton-like reactions under conditions convenient for practical application, i.e. near ambient conditions and nearly neutral to slightly acidic pH range. The catalytic activity of the perovskites was evaluated with respect to achievable degradation rates for two model contaminants (phenol and methyl *tert*-butyl ether, MTBE) and H_2O_2 utilization. The influence of the employed reaction conditions, in particular H_2O_2 and catalyst concentrations, reaction pH and temperature, on contaminant degradation, as well as on the stability and reusability of the catalyst, were studied. Additionally, isotope fractionation studies were carried out in order to assess the possible reaction pathways in the perovskite-catalyzed oxidation.

2. Experimental part

2.1. Chemicals and materials

Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), ethylene glycol, 2-methoxy-methanol, nitric acid, *n*-hexane, *d*₅-phenol, phenol, MTBE, ethyl *tert*-butyl ether (ETBE) and H_2O_2 (30 wt.%) were obtained from Sigma Aldrich or Merck, Germany, with the highest purity, and used as received. Titanium(IV) oxysulfate solution (1.9–2.1%) for determination of H_2O_2 was obtained from Fluka, Germany.

2.2. Synthesis of LFO

LFO was prepared by the sol–gel method following the procedure reported in [22]. 0.01 mol $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.01 mol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100 mL deionized water in a 200 mL glass beaker and placed on a magnetic stirrer. 0.01 mol of citric acid was added as complexant. The resulting yellowish-brown sol was heated to 80 °C for 12 h in order to induce gel formation. Afterwards, the sample was placed in a muffle furnace and calcined at 600 °C for 2 h. Thereafter, the temperature was raised to 800 °C at 5 K min^{-1} and kept constant for 2 h.

2.3. Synthesis of BFO

BFO was synthesized according to a modified sol–gel method as described in [19]. 0.01 mol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.01 mol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were dissolved in 25 mL 2-methoxymethanol in a 50 mL glass beaker followed by adding 20 μL HNO_3 . The mixture was placed on a magnetic stirrer and 0.01 mol citric acid (as complexant) and 15 mL ethylene glycol (as dispersant) were added. The resulting mixture was heated to 100 °C for 10 h to obtain a dark viscous resin. Afterwards, the sample was placed in a muffle furnace heated to 550 °C (5 K min^{-1}) and calcined for 2 h at this temperature.

2.4. Characterization of the catalyst

X-ray diffraction (XRD) analysis was used in order to identify the crystal structure of the prepared solid catalysts. XRD patterns were recorded on a Bruker D8 Diffractometer at room temperature using $\text{Cu K}\alpha$ radiation. Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FT-IR) spectra were collected at room temperature using a Bruker Tensor 27 spectrometer equipped with a diamond ATR unit. TEM images were obtained with a Jeol 1011 (Jeol

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