



# Lanthanide perovskite catalysts for oxidation of chloroaromatics: Secondary pollution and modifications



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## ABSTRACT

Chlorobenzene (CB) was selected as a representative chloroaromatic to evaluate its oxidation process over a perovskite LaMnO<sub>3</sub> catalyst. It was noted that in catalytic CB oxidation, severe deactivation occurred in the LaMnO<sub>3</sub> catalyst. This was mainly ascribed to surface coke deposition (involving long-chain organics) and the loss of redox ability. The byproducts in the oxidation process involved certain polychlorinated chain organics of C<sub>2</sub>OCl<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub>, and C<sub>2</sub>Cl<sub>4</sub>, which were believed to be generated through nucleophilic substitution at the Lewis acid sites of exposed MnCl<sub>x</sub> or MnO<sub>y</sub>Cl<sub>z</sub>. Modification of LaMnO<sub>3</sub> by introduction of CeO<sub>2</sub> and HF etching was found to distinctly retard catalyst deactivation. The loaded CeO<sub>2</sub> with enriched oxygen vacancies reduced coke deposition and retained the redox ability of LaMnO<sub>3</sub>. The HF etching forced the fluoride ions (F<sup>-</sup>) to replace the surface lattice oxygen, which significantly promoted the mobility of surf-O<sub>latt</sub> and bulk-O<sub>latt</sub> and facilitated Cl desorption (via a Deacon reaction mechanism) from the catalyst surface, ensuring superior oxidation efficiency and stability for catalytic chloroaromatics oxidation. As calculated, the TOF of investigated catalysts followed the sequence LaMnO<sub>3</sub>-CeO<sub>2</sub>-HF (11.58 × 10<sup>-5</sup> s<sup>-1</sup>) > LaMnO<sub>3</sub>-CeO<sub>2</sub> (10.14 × 10<sup>-5</sup> s<sup>-1</sup>) > LaMnO<sub>3</sub> (5.44 × 10<sup>-5</sup> s<sup>-1</sup>) at 120 °C in catalytic CB oxidation.

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## 1. Introduction

Chloroaromatics are a class of highly toxic volatile organic compounds (VOCs) that can be emitted from the coking industry, secondary nonferrous metallurgical facilities, and municipal solid waste incinerators (MSWIs) [1,2]. The catalytic combustion route for chloroaromatics elimination often unintentionally converts the chloroaromatics into unexpected polychlorinated byproducts, such as biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs) [3,4]. This conversion process involves a surface-mediated reaction and can be accelerated in the presence of a catalyst. The oxidation of chloroaromatics over an applied catalyst generally involves four steps: Cl dissociation, aromatic ring cleavage, chain hydrocarbon deep oxidation, and Cl desorption/accumulation [5–8]. The desorption of Cl plays a crucial role and determines the conversion efficiency of chloroaromatics. It also dominates the formation of

PCB, PCDDs, and PCDFs [9,10] because, if the dissociated Cl species are not desorbed in time, the accumulated Cl tends to react with the aromatic ring (via nucleophilic substitution at oxygen vacancies, noble metals, or Brønsted acidic sites [5,8,11]) to form polychlorinated aromatic hydrocarbons. These polychlorinated aromatic hydrocarbons will then transform into chlorophenoxyl radicals, which are considered to be the dominant precursors for the formation of PCDDs and PCDFs [10,12–14].

In the literature, metal oxides (e.g., CuO, Fe<sub>2</sub>O<sub>3</sub> [15,16]), noble metals (Pt, Pd [11,17,18]), and zeolite-based catalysts (Mn<sub>1-x</sub>Ce<sub>x</sub>O<sub>2</sub>/HZSM-5 [5]) have been verified to be capable of inducing a nucleophilic substitution reaction to produce unexpected polychlorinated byproducts in chloroaromatics oxidation. As widely utilized industrial catalysts [19,20], lanthanide perovskite oxides (e.g., LaCO<sub>3</sub>, LaMnO<sub>3</sub>, and LaCrO<sub>3</sub>) have been studied solely for their conversion efficiency for chloroaromatics oxidation [21,22] (where few studies have been related to HCl and CO<sub>2</sub> selectivity [23]), in which the possible formation of unexpected byproducts has not been investigated. We evaluated the chloroaromatics oxidation process (choosing chlorobenzene (CB) as a representative) over perovskite LaMnO<sub>3</sub> to identify the CB oxidation efficiency/selectivity, the intermediate byproducts, the possible formation of PCDDs

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and PCDFs, the deactivation mechanism for recovery, and the surface accumulation compounds (after aging) for waste disposal. Modifications of  $\text{LaMnO}_3$  toward improved oxidation efficiency and generation of fewer byproducts by introducing a co-catalyst and HF etching were also explored. Our goal in this work is to obtain a better understanding of the lanthanide perovskites as catalysts for chloroaromatics oxidation, aiming to elucidate design strategies for catalysts with less secondary pollution and high durability in industrial applications.

## 2. Experimental

### 2.1. Catalyst preparation

In a typical supercritical water (sc- $\text{H}_2\text{O}$ ) synthesis process (see Fig. S1 in the Supporting Information), the metal nitrate solution (containing  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 50% $\text{Mn}(\text{NO}_3)_2$ , and  $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with a total of 0.2 mol/L) and  $\text{NaOH}$  (0.5 mol/L) were separately pumped into the reactor using HPLC pumps over a range of flow rates, including 6, 7, and 7.5  $\text{mL} \cdot \text{min}^{-1}$ . The two streams were mixed in a stainless steel Swagelok 1/8" tee piece at room temperature, and were then carried to meet a stream of deionized water that was fed by another HPLC pump at certain flow rates (e.g., 25 and 30  $\text{mL} \cdot \text{min}^{-1}$ ) and heated beyond the supercritical temperature (374 °C) using an electric furnace. An adjustable-length band heater set to 500 °C was added to the reactor to maintain the reaction temperature. The suspension was washed with distilled water till neutral pH was reached. Solids were recovered by centrifuging the suspension and then freeze-dried to obtain brown powders. The precursors were subsequently heated in static air at 700 °C for 2 h to yield  $\text{LaMnO}_3$  and at 750 °C for 3 h to obtain  $\text{LaMnO}_3\text{-CeO}_2$ . Acid etching was performed by immersing  $\text{LaMnO}_3\text{-CeO}_2$  (2 g) in 0.1 M HF (50 mL) for 30 min at room temperature. Then the sample was washed by deionized water to pH 7, dried at 120 °C overnight, and calcined at 400 °C for 2 h.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcat.2018.07.022>.

### 2.2. Catalyst characterizations

XRD patterns were recorded using a Rigaku D/Max RA diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) at 40 kV and 150 mA; the crystal phase of the sample was identified using the JCPDS database. To analyze the morphology of the crystals, a Model FEI Tecnai F20 high-resolution transmission electron microscope (HR-TEM, 400 kV accelerating voltage), equipped with an energy-dispersive X-ray spectrometer (EDS) was employed. The BET surface areas (SBET) were determined using  $\text{N}_2$  physical adsorption at 77 K with a Micromeritics ASAP 2020 apparatus. Samples were subjected to a pretreatment process at 150 °C for 2 h under vacuum. Surface elemental analysis was conducted using a Thermo ESCALAB 250 XPS instrument with  $\text{AlK}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ) operating at 150 W. The signal of adventitious carbon (a binding energy of 284.8 eV) was used to calibrate the binding energy scale. Curve fitting were performed using a Shirley background and a Gaussian peak shape with 20% Lorentzian character.

$\text{O}_2$  TPD was conducted in a TP-5089 supplied by Tianjin Xianquan Industry and Trade Development Co. Prior to the test, 0.1 g of sample was preheated at 400 °C for 2 h under  $\text{O}_2$  atmosphere (at a rate of 30  $\text{mL} \cdot \text{min}^{-1}$ ), and was then slowly cooled down to 100 °C. Thereafter, it was swept with pure He with a flow rate of 30  $\text{mL} \cdot \text{min}^{-1}$  for 1.5 h and then heated from 100 to 900 °C. The signal of desorbed oxygen was recorded by a mass spectrometer (Hiden Analytical, Ltd.) and calibrated by a pulse of pure  $\text{O}_2$  with volume 1 mL. In brief, a pulse of 1 mL pure oxygen was first purged

into the mass spectrometer, leading to the appearance of an  $\text{O}_2$  desorption spectrum. By integrating the oxygen MS signal with time, we obtained the peak area corresponding to 1 mL pure oxygen.

$\text{H}_2$  TPR was conducted in a TP-5089 (supplied by Tianjin Xianquan Industry and Trade Development Co.). Samples (0.05 g) were preheated to 400 °C for 1 h and cooled to 100 °C with a purge of 5%  $\text{O}_2/\text{He}$  gas (30  $\text{mL} \cdot \text{min}^{-1}$ ). Then the samples were preheated at 100 °C for 40 min and further heated to 900 °C at a rate of 10  $^\circ\text{C} \cdot \text{min}^{-1}$  in a purge of 5%  $\text{H}_2/\text{N}_2$  gas at a flow rate of 35  $\text{mL} \cdot \text{min}^{-1}$ . The signals of consumed  $\text{H}_2$  were recorded using a thermal conductivity detector (TCD).  $\text{H}_2$  consumption was calculated by the complete reduction of a known standard of powdered  $\text{CuO}$ .

$\text{NH}_3$  TPD was also performed in TP-5089 (supplied by Tianjin Xianquan Industry and Trade Development Co.). Prior to the test, 0.1 g samples were pretreated at 400 °C for 2 h under pure He. The samples then preadsorbed 6% $\text{NH}_3/\text{N}_2$  (30  $\text{mL} \cdot \text{min}^{-1}$ ) at 80 °C for 1 h and slowly heated to 100 °C. Subsequently, the samples were swept with pure He with a flow rate of 30  $\text{mL} \cdot \text{min}^{-1}$  for 2 h and then heated from 100 to 900 °C. The signals of desorbed  $\text{NH}_3$  were recorded by a quadrupole mass spectrometer (Hiden Analytical, Ltd.).

$\text{NH}_3$  DRIFT measurements were performed with ZnSe windows coupled to Bruker Tensor 27 FTIR spectrometers. In the DRIFT cell, catalysts were pretreated at 400 °C under He for 2 h, and then cooled to 150 °C. The background spectrum was recorded with flowing He and subtracted from the catalyst spectrum.

The outlet by-products (containing various gaseous organics) were captured using an adsorption tube (Tenax TA/Tenax GR) at the given temperatures for 30 min. These adsorbents were then desorbed in a thermal desorption instrument (TDI, PERSEE-TP7) and analyzed using a GC/MS system (Agilent 7890A GC equipped with an Agilent 5975C MS) with a J&W113-4332GS-GasPro chromatographic column. The surficial accumulation compounds of used catalysts were tested by heating the catalysts at 350 °C in a thermal desorption instrument and analyzed using GC-MS.

### 2.3. Catalytic activity measurement

Catalytic activity tests were conducted in a continuous fixed-bed quartz microreactor (i.d. 8 mm) placed in a tubular furnace. To minimize the hot-spot effect, quartz sands (40–60 mesh) were mixed with 0.5 g of catalyst (40–60 mesh) and the total volume of the catalysts was kept at 1 mL. The total flow rate of the mixed reactant gas (1000 ppm CB + 10%  $\text{O}_2 + \text{N}_2$ ) was set to 166  $\text{mL} \cdot \text{min}^{-1}$ , aiming to maintain a weight hourly space velocity (WHSV) of 20,000  $\text{mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ . A blank experiment with only quartz sands was conducted, and no CB conversion was observed under 400 °C, indicating that the CB could not be oxidized under the selected conditions without a catalyst. Considering that the catalysts would suffer Cl poisoning along with the testing, each data point was obtained by analyzing the effluent gases at a given temperature (maintained for 25 min) online using GC. This was expected to guarantee a steady state for the measurements because the outlet CB concentration tended to be stable at approximately 25 min. All the CB conversion tests were conducted at least three times in order to check the experimental error, which was lower than 2% in all temperature ranges. The conversion of CB ( $X_{\text{CB}}$ ) was calculated as  $X_{\text{CB}} = [C_{\text{CB}(\text{in})} - C_{\text{CB}(\text{out})}] / C_{\text{CB}(\text{in})} \times 100\%$ , where  $C_{\text{CB}(\text{in})}$  and  $C_{\text{CB}(\text{out})}$  represented the CB concentrations in the inlet and outlet gas, respectively. The  $\text{CO}_2$  selectivity ( $S_{\text{CO}_2}$ ) of the catalysts was calculated by  $S_{\text{CO}_2} = C_{\text{CO}_2(\text{out})} / 6 \times C_{\text{CB}(\text{in})} \times 100\%$ , where  $C_{\text{CO}_2(\text{out})}$  represented the  $\text{CO}_2$  concentration in the outlet gas.

The reactants and products were analyzed using a gas chromatograph (Agilent Technologies 7890A GC) equipped with a flame ionization detector (FID) and a thermal conduction detector

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