



Short communication

# La<sub>0.8</sub>M<sub>0.2</sub>MnO<sub>3</sub> (M = Ba, Ca, Ce, Mg and Sr) perovskite catalysts for plasma-catalytic oxidation of ethyl acetate

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## ABSTRACT

Plasma-catalytic removal of low concentration ethyl acetate was carried out over La<sub>0.8</sub>M<sub>0.2</sub>MnO<sub>3</sub> (M = Ba, Ca, Ce, Mg and Sr) catalysts prepared by sol-gel method using citric acid as a mixing complex. The La<sub>0.8</sub>Ce<sub>0.2</sub>MnO<sub>3</sub> catalyst showed the highest removal of ethyl acetate and CO<sub>2</sub> selectivity over the specific energy density (SED) range followed by the La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> catalyst, while Ba, Ca and Mg-doped catalysts inhibited the oxidation of ethyl acetate compared to the pure LaMnO<sub>3</sub> catalyst. A wide range of catalyst characterization including N<sub>2</sub> adsorption-desorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) indicated that the reducibility of the catalysts played an important role in determining the reaction performance of the plasma-catalytic gas cleaning process.

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## 1. Introduction

Volatile organic compounds (VOCs) are considered as a major contributor to air pollution and may cause health issues to humans. Great efforts have been devoted to the research and development of VOC abatement technologies in order to meet air quality standards [1]. During the last three decades, non-thermal plasma (NTP) technology has shown great potential for removal of low concentration VOCs in large volume waste gas streams due to its unique ability to generate a chemically reactive environment even at room temperature [2,3]. However, the main disadvantages of NTP technology for the removal of VOCs are the formation of undesirable by-products in the plasma process and the relatively low energy efficiency. The combination of NTP and catalysis (“plasma-catalysis”) provides a promising solution to overcome these problems. The interaction of the plasma and catalysts could generate a synergistic effect and affect the performance of plasma processing of VOCs, for example by improving the removal efficiency and CO<sub>2</sub> selectivity, and reducing the formation of by-products [4–6].

Up until now, various kinds of catalysts have been tested in the plasma-catalytic removal of VOC pollutants. Noble metal catalysts have shown excellent performance in VOC oxidation [7,8]. However, the high cost and low poisoning resistance of noble metal catalysts limits their industrial application. Recently, transition metal catalysts have been intensively investigated due to their relatively low cost and poison

resistance [4,9,10]. Among these catalysts, special attention has been paid to perovskite-type catalysts, especially LaMnO<sub>3</sub> catalysts due to their thermal stability, mixed valence states of the transition metals and oxygen mobility [11–13]. Dinh et al. reported that the removal efficiency of trichloroethylene was increased from 68% to 88% at a specific energy density (SED) of 460 J L<sup>-1</sup> in a two-stage plasma-catalysis configuration [14]. Vandenbroucke et al. also reported that the removal of trichloroethylene was improved by 25% when a Pd/LaMnO<sub>3</sub> catalyst was placed downstream of the plasma compared to that achieved when using plasma alone at a SED of 300 J L<sup>-1</sup> [15]. Partial substitution of the A-site in the perovskite structure of LaMnO<sub>3</sub> could change the catalyst structure and in turn affect the catalytic oxidation of pollutants including NO [16,17], chlorobenzene [11], vinyl chloride [18] and butane [19], etc. However, no work has been done on the use of A-site substituted LaMnO<sub>3</sub> catalysts in plasma-catalytic removal of VOCs. It is not clear about the roles of the substitutes in the plasma-catalytic oxidation process.

In this work, ethyl acetate was chosen as the model pollutant since it is widely used as a solvent in the chemical industry. A series of A-site substituted LaMnO<sub>3</sub> catalysts (M = Ba, Ca, Ce, Mg and Sr) were synthesized using sol-gel method and tested in a coaxial dielectric barrier discharge (DBD) reactor. Catalysts can be easily integrated into a DBD reactor as a hybrid plasma-catalytic process for the destruction of gas pollutants such as VOCs. In addition, DBD systems have been extensively used for ozone generation on an industrial scale and have great potential to be scaled up for the gas cleaning process. The role of the substitutes on the reaction performance was proposed based on the results of catalyst characterization.

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## 2. Experimental

### 2.1. Catalyst preparations

The  $\text{La}_{0.8}\text{M}_{0.2}\text{MnO}_3$  ( $\text{M} = \text{Ba}, \text{Ca}, \text{Ce}, \text{Mg}$  and  $\text{Sr}$ ) perovskite type catalysts were prepared by sol-gel method using citric acid as the complexing agent. All chemicals were of analytic reagent grade. Metal nitrates were dissolved and mixed in deionized water to get solutions with the concentration of 0.1 M. Then, citric acid with an excess molar ratio of 50% (compared to the total metal cations) was added to the above solution as a ligand. The solution was thoroughly stirred and evaporated in a water bath (80 °C) to get viscous gel. The obtained sample was dried at 110 °C overnight and calcined at 700 °C for 5 h. The synthesized samples were sieved to 35–60 meshes. Pure  $\text{LaMnO}_3$  was prepared using the same method.

### 2.2. Catalyst characterization

The  $\text{N}_2$  adsorption-desorption experiments were carried out using a Quantachrome Autosorb-1 instrument at  $-196$  °C. The X-ray diffraction (XRD) patterns of the catalysts were analyzed by a Rigaku D/max-2000 X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo ESCALAB 250 instrument equipped with an Al  $\text{K}\alpha$  X-ray source at 150 W. Temperature-programmed reduction with hydrogen ( $\text{H}_2$ -TPR) was carried out using a gas chromatograph (Kexiao 1690) equipped with a thermal conductivity detector (TCD) to determine the reducibility of the samples.

### 2.3. Plasma-catalytic system

The details of the plasma-catalytic system have been described in our previous work [20]. A stainless steel mesh (ground electrode) 60 mm in length was tightly wrapped around of a quartz tube with an inner diameter of 8 mm and wall thickness of 1 mm. A stainless steel rod (2 mm in diameter) was used as a high voltage electrode and placed along the axis of the quartz tube. In each experiment, 100 mg of catalyst was packed inside the plasma region and held with quartz wool. The catalysts were pretreated in a  $\text{N}_2$  flow for 1 h before each test. The DBD reactor was connected to an AC high voltage power supply (CTP-2000, Suman) at 10 kHz. The electrical signals of the plasma were recorded using a digital oscilloscope (Tektronix 4034B). The discharge power was calculated using the Q-U Lissajous method. The total gas flow rate was 1  $\text{L min}^{-1}$ , made up of 100 ppm ethyl acetate, 20%  $\text{O}_2$  and  $\text{N}_2$  in balance. Thus, the specific energy density was defined as

$$SED \left( \text{J} \cdot \text{L}^{-1} \right) = \frac{P \left( \text{W} \right)}{Q \left( \text{L} \cdot \text{min}^{-1} \right)} \times 60 \quad (1)$$

where  $P$  is the discharge power and  $Q$  is the gas flow rate.

The gas compositions (ethyl acetate, CO and  $\text{CO}_2$ ) in the effluent were measured using a Gasetm Dx4000 FT-IR gas analyzer with an accuracy of  $\pm 3\%$ . All measurements were carried out when the outlet gas composition reached equilibrium. The conversion of ethyl

acetate ( $\eta_{\text{ethyl acetate}}$ ) and  $\text{CO}_2$  selectivity ( $S_{\text{CO}_2}$ ) of the plasma-catalytic process were defined as

$$\eta_{\text{ethyl acetate}} = \frac{c_{\text{in}} - c_{\text{out}}}{c_{\text{in}}} \times 100\% \quad (2)$$

$$S_{\text{CO}_2} = \frac{c_{\text{CO}_2}}{c_{\text{CO}} + c_{\text{CO}_2}} \times 100\% \quad (3)$$

where  $c_{\text{in}}$  and  $c_{\text{out}}$  are the inlet and outlet concentrations of ethyl acetate, respectively, while  $c_{\text{CO}}$  and  $c_{\text{CO}_2}$  are the concentration of outlet CO and  $\text{CO}_2$ .

## 3. Results and discussion

### 3.1. Structure of the catalysts

Table 1 summarizes the physicochemical properties of the  $\text{La}_{0.8}\text{M}_{0.2}\text{MnO}_3$  catalysts. The specific surface area ( $S_{\text{BET}}$ ) and pore volume of the  $\text{LaMnO}_3$  catalyst were 14.4  $\text{m}^2 \cdot \text{g}^{-1}$  and 0.107  $\text{cm}^3 \cdot \text{g}^{-1}$ , respectively. The substitution of La with the dopants slightly decreased the  $S_{\text{BET}}$  and pore volume except for the  $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$  catalyst, which had a surface area of 17.0  $\text{m}^2 \cdot \text{g}^{-1}$  and a pore volume of 0.113  $\text{cm}^3 \cdot \text{g}^{-1}$ .

The XRD patterns of the catalysts present the typical diffraction peaks of rhombohedral  $\text{LaMnO}_3$  (JCPDS 50-0298) with characteristic peaks at  $2\theta = 23.0^\circ, 32.5^\circ, 40.1^\circ, 46.9^\circ, 58.1^\circ, 68.6^\circ$  and  $77.8^\circ$  (Fig. 1). No obvious diffraction peaks for impurities like  $\text{La}_2\text{O}_3$  and  $\text{MnO}_x$  were detected. The crystalline structure of  $\text{LaMnO}_3$  was maintained after partial substitution of lanthanum. However, the main characteristic peak at  $32.5^\circ$  slightly shifted to a higher  $2\theta$  value when  $\text{La}^{3+}$  was substituted by  $\text{Mg}^{2+}$  and  $\text{Ce}^{4+}$ . This could be attributed to the difference in the ion radicals of these species as the ion radius of  $\text{La}^{3+}$  (1.06 Å) was larger than that of  $\text{Mg}^{2+}$  (0.71 Å) and  $\text{Ce}^{4+}$  (1.01 Å) [21]. Similarly, when La was substituted by ions with larger radius such as  $\text{Ca}^{2+}$  (1.14 Å),  $\text{Sr}^{2+}$  (1.32 Å) and  $\text{Ba}^{2+}$  (1.49 Å), the characteristic peak at  $32.5^\circ$  shifted to a lower  $2\theta$  value. This phenomenon also indicated the incorporation of the dopants into the perovskite lattice. The difference of ion radicals between  $\text{La}^{3+}$  and the dopants could change the lattice volume and form defects in the perovskite structure [22].

The particle size of the catalyst was calculated using Scherrer's equation based on the (200) crystal face at around  $32.5^\circ$ . The crystallite size of the catalysts decreased after partial substitution, while the  $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$  catalyst showed the smallest crystal size of 14.0 nm. The crystallite size of other  $\text{La}_{0.8}\text{M}_{0.2}\text{MnO}_3$  catalysts was in a narrow range of 15.9–16.6 nm, and followed the same trend as the ion radius. This phenomenon indicated that the crystalline growth was restrained by the incorporation of the dopants, which was beneficial for the oxidation of ethyl acetate over the catalyst surface.

### 3.2. Redox properties of the catalysts

The XPS spectra of O 1s are shown in Fig. 2. Three major components were identified by deconvoluting the peaks between 528 eV to 535 eV.

**Table 1**  
Physicochemical properties of the catalysts.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	Pore volume ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	Crystallite size (nm) <sup>a</sup>	$\text{O}_{\text{ads}} / (\text{O}_{\text{ads}} + \text{O}_{\text{lat}})$ (%)	$\text{H}_2$ consumption ( $\mu\text{mol} \cdot \text{g}^{-1}$ ) ( $T < 600$ °C)
$\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$	11.9	0.097	16.2	38.9	3.73
$\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$	10.8	0.088	15.9	40.4	4.51
$\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$	17.0	0.113	14.0	47.5	5.26
$\text{La}_{0.8}\text{Mg}_{0.2}\text{MnO}_3$	12.7	0.086	15.9	42.3	4.02
$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	13.4	0.087	16.6	45.1	3.83
$\text{LaMnO}_3$	14.4	0.107	16.8	38.2	3.52

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