



Enhanced performance for plasma-catalytic oxidation of ethyl acetate over $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ catalysts



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ABSTRACT

In this work, plasma-catalytic oxidation of low concentration ethyl acetate (100 ppm) over $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ ($x=0, 0.05, 0.1, 0.3$ and 0.5) perovskite catalysts was carried out in a coaxial dielectric barrier discharge (DBD) reactor. The effects of Ce-doping on the removal of ethyl acetate and CO_x ($x=1$ and 2) selectivity in the plasma-catalytic oxidation process were investigated as a function of specific energy density (SED). Compared to the plasma reaction without a catalyst, the presence of the LaCoO_3 catalyst in the plasma enhanced the removal of ethyl acetate and CO_x selectivity. The use of the Ce-doped catalysts further enhanced the performance of the plasma-catalytic oxidation process. The highest removal efficiency of ethyl acetate (100%) and CO_x selectivity (91.8%) were achieved in the plasma-catalytic oxidation of ethyl acetate over the $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3+\delta}$ catalyst at a SED of 558 J L^{-1} . The interactions between Ce and LaCoO_3 resulted in an increased specific surface area (by 17.1%–68.6%) and a reduced crystallite size (by 13.5%–68.2%) of the Ce-doped LaCoO_3 catalysts compared to pure LaCoO_3 , which favours the oxidation of ethyl acetate in the plasma process. Compared to the LaCoO_3 catalyst, the Ce-doped perovskite catalysts showed higher content (maximum 54.9%) of surface adsorbed oxygen (O_{ads}) and better reducibility, both of which significantly contributed to the enhanced oxidation of ethyl acetate and intermediates in the plasma-assisted surface reactions. The coupling of plasma with the Ce-doped catalysts also reduced the formation of by-products including NO_2 and N_2O . The possible reaction pathways involved in the plasma oxidation process have been discussed.

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1. Introduction

Ethyl acetate is an organic ester compound, commonly used as a solvent for cleaning electric circuit boards, paint removal and coating. Ethyl acetate easily evaporates, resulting in a large amount being released into the environment, which could cause health problems. Exposure to ethyl acetate even at low concentration may cause nausea, dizziness, irritation and even cancer. Currently, incineration and catalytic oxidation have been the most widely used technologies for the removal of ethyl acetate. However, these technologies are not cost-effective when dealing with the abatement of low concentration ethyl acetate contained in high volume waste gas streams due to the requirement of externally heating large volumes of gas.

Non-thermal plasma (NTP) has been regarded as a promising and attractive alternative to conventional technologies for the removal of a range of low concentration volatile organic compounds (VOCs) in waste gas streams [1,2]. Energetic electrons and highly reactive species including O, O_3 , N and N_2 excited states could be generated in an air NTP even at room temperature, while these energetic species are capable of initiating a variety of chemical reactions, involving direct and indirect destruction of pollutants and intermediates. However, the main challenges in the use of NTP for gas clean-up are the formation of hazardous organic by-products and the relatively low energy efficiency of the plasma process [3,4].

The combination of non-thermal plasma and heterogeneous catalysis has shown great potential to overcome the disadvantages of using NTP alone for gas clean-up and purification. The presence of the catalysts in the plasma could potentially extend the discharge region, offering extra adsorption and active sites for the oxidation of ethyl acetate and driving the reactions with reduced formation of undesirable by-products. This could consequently enhance

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the overall performance of the plasma-catalytic oxidation of ethyl acetate in terms of the removal efficiency of ethyl acetate, product selectivity and energy consumption [5,6].

Perovskite-type oxide catalysts have been widely used in thermal catalytic reactions due to their comparative catalytic activity, high thermal stability and low cost. However, very limited perovskite-type catalysts have been explored and investigated in low temperature plasma-catalytic reactions for either gas cleaning or the synthesis of fuels and chemicals. Sun et al. reported that the removal efficiency of toluene was enhanced by ~25% in a $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ catalyst packed dielectric barrier discharge (DBD) reactor at an applied voltage of 21.5 kV compared to that achieved in the reaction using plasma-alone [7]. Dinh et al. also found that the removal of trichloroethylene was increased by over 15% when placing a LaMnO_3 catalyst in a plasma reactor at a specific energy density (SED) of 300 J L^{-1} , while the CO_2 selectivity was slightly enhanced [3]. Pahn et al. reported that the reaction selectivity and carbon balance of plasma methane conversion was considerably enhanced when operating in the temperature range from room temperature to 400°C in the presence of a LaAlO_3 catalyst [8].

Recent studies pointed out that partial substitution of A-site of the perovskite catalysts by cations with different oxidation states could result in the formation of structural defects in the catalysts, changing the redox properties of the catalysts and consequently enhancing the catalytic activity. The most popular substitutes for A-site are rare earth, alkali or alkaline earth metals including Sr, Ce, K, Ca and Ba, etc. [9–12]. Among these metals, cerium (Ce) has been widely used as a promoter for catalytic oxidation of VOCs due to its excellent oxygen storage capacity and redox properties between different valences. Previous works have demonstrated that the incorporation of Ce into various perovskite-type catalysts benefits the catalytic oxidation of a variety of pollutants including vinyl chloride [12], benzene [13], methane [14] and even soot [15]. However, the application of Ce-doped perovskite-type catalysts in plasma-induced oxidation of VOCs to enhance the reaction performance of the plasma-catalytic process has not been reported to the best of our knowledge.

In this work, the effect of Ce-doped LaCoO_3 catalysts on the plasma-catalytic oxidation of ethyl acetate (100 ppm) was investigated in terms of the removal efficiency of ethyl acetate, CO_x ($x = 1$ and 2) selectivity and by-product formation in a cylindrical DBD reactor. A range of catalyst characterization, including Brunauer-Emmett-Teller (BET) surface measurement, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction of H_2 (H_2 -TPR), was performed to get a better understanding of the interactions between Ce-doping and LaCoO_3 catalyst and the roles of Ce-doping in the plasma-catalytic oxidation process. The formation of by-products in the plasma-catalytic oxidation process and possible reaction mechanisms behind the plasma oxidation reaction has also been discussed.

2. Experimental

2.1. Catalyst preparation

The $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ ($x = 0, 0.05, 0.1, 0.3$ and 0.5) perovskite type catalysts were prepared by sol-gel method using citric acid as complexing agent and nitrate salts (La, Ce and Co) as precursors. All chemicals were analytic reagent grade (Aladdin Ltd). The desired amount of metal nitrates were firstly dissolved and mixed in deionized water to get 0.1 M solutions. Citric acid with an excess molar ratio of 50% (compared to metal cations) was added to the above solution as a ligand. The solution was vigorously stirred and evaporated in a water bath (80°C) to get viscous gel. The obtained sample was then dried in an oven at 110°C overnight followed by calcina-

tion at 700°C for 5 h. The catalyst samples were pressed and sieved to 35–60 meshes.

2.2. Catalyst characterization

The structural properties of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ catalysts including specific surface area, average pore size and pore volume were determined via N_2 adsorption-desorption experiments using a Quantachrome Autosorb-1 instrument at -196°C (77 K). Prior to each measurement, the catalyst samples were degassed at 200°C for 5 h. The XRD patterns of the catalysts were analyzed by a Rigaku D/max-2000 X-ray diffractometer. The instrument was equipped with a $\text{Cu-K}\alpha$ radiation source, while the scan was conducted in the 2θ range from 10° to 80° with a step size of 0.02° . X-ray photoelectron spectroscopy experiments were performed with a Thermo ESCALAB 250 instrument equipped with an $\text{Al K}\alpha$ X-ray source ($h\nu = 1486.6\text{ eV}$) at 150 W. Sample charging effect was calibrated by correcting the obtained spectra with the C 1s binding energy (B.E.) value of 284.6 eV. The relative concentrations of cerium ions and oxygen species were calculated based on the areas of the corresponding peaks derived from the XPS spectra of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ catalysts. The reducibility of the $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ catalysts was determined by H_2 -TPR using a chemisorption analyzer (Micromeritics, Autochem II 2920). For each test, 50 mg catalyst samples were pre-treated at 250°C in a N_2 flow for 1 h and cooled down to room temperature. The samples were then heated to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ with a 5 vol.% H_2/Ar flow at a flow rate of 40 mL min^{-1} . The amount of consumed H_2 was calculated by the integration of the peaks in the H_2 -TPR profiles.

2.3. Experimental set-up

The experimental set-up consisted of a gas supply system, a DBD reactor, a high voltage power supply, and gas analysis instruments (Fig. 1). Zero grade air (99.999%, Jingong, Hangzhou) was used as a carrier gas in this work. Gaseous ethyl acetate was generated from a gas cylinder (0.5% ethyl acetate, balanced air). All gas streams were regulated by mass flow controllers (Sevenstars D07B, China) and premixed in a mixing chamber before being injected into the DBD reactor. Typically, the experiments were carried out at a total flow rate of 1 L min^{-1} , while the initial concentration of ethyl acetate was 100 ppm. The geometry of the DBD reactor has been described in detail elsewhere [16]; the discharge gap was fixed at 4 mm in this work. 100 mg $\text{La}_{1-x}\text{Ce}_x\text{CoO}_{3+\delta}$ catalyst sample was placed in the plasma region and held in place by quartz wool before each experiment. The length of the catalyst bed was 5 mm. The reactor was connected to an AC high voltage power supply (Suman CTP2000-K, China).

The applied voltage was measured by a high voltage probe (1000:1, Tektronix 6015A), while the voltage across the external capacitor ($0.47\ \mu\text{F}$) was monitored by a voltage probe (Tektronix TPP500). All the electrical signals were sampled by a four-channel digital oscilloscope (Tektronix 3034B). The discharge power was calculated using Q-U Lissajous method. The specific energy density of the plasma process is defined as follows:

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

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

Gas analysis was performed by an online multi-component analyzer (Gasmeter Dx4000, Finland) with a resolution of 8 cm^{-1} . The analyzer was calibrated with a standard ethyl acetate gas prior to use. The effective path length of the analyzer was 5 m, while the volume of the gas cell was 0.4 L. Measurements were carried out after running the plasma system for about 40 min, when a steady-state had been reached. All the measurements were repeated three

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