



# A strategy for improving deactivation of catalytic combustion at low temperature via synergistic photocatalysis



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## ARTICLE INFO

### Article history:

Received 5 September 2014

Received in revised form 11 October 2014

Accepted 14 October 2014

Available online 23 October 2014

### Keywords:

Photocatalysis  
Catalysis synergy  
Remediation  
Air purification  
Surface hydroxyl

## ABSTRACT

For practical catalytic combustion in heterogeneous catalysis, non-noble metal oxides with excellent low temperature activity as well as performance sustainability still remain challenging. Herein, semiconductor photocatalysis was introduced to address the problems. With greatly enhanced spectral response and low temperature reducibility,  $\text{MnO}_x\text{-CeO}_2$  mixed oxide achieved convincing photo/thermo-catalysis synergy in formaldehyde abatement. This synergy is promising for utilizing infrared (IR) energy from sunlight and idle heat from daily illuminants. Moreover, the exhausted material after prolonged dark reaction presented inspiring self-remediation under in situ light irradiation. Catalytic cycles were thoroughly studied, unveiling the underlying mechanism based on photo-induced remediation. Roles of high valence metal ions, reaction intermediates and surface hydroxyls ( $-\text{OH}$ ) have been in-depth and newly cognized. Given the day and night alternations in nature, our results may be instructive in designing reliable catalysts for efficient and sustainable catalytic combustion.

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## 1. Introduction

Under consideration of both human health and environmental legislation, catalytic combustion of volatile organic compounds (VOCs) using transition metal oxides has been highly promising because of its technical and economic feasibility [1–5]. Recently, many efforts have been devoted to bringing down the starting temperature of various catalytic processes [6–8], as well as regenerating the exhausted catalyst after deactivation [9–12]. However, for the present the low temperature activity is still limited. Besides, additional post-treatments are generally required for material regeneration. For instance,  $\text{O}_2/\text{Ar}$  purging at  $250^\circ\text{C}$  and oxalic acid washing have been proposed to recover the used  $\text{Co}_3\text{O}_4$  and three way catalysts (TWCs), respectively [10,13]. These requirements cannot be easily fulfilled and greatly hinder related civilian applications. A mild, convenient and in situ catalyst remediation for daily and practical VOCs abatement still remains a challenge.

During past decades, semiconductor photocatalysis has been widely attractive in environmental purification as well as artificial photosynthesis [14–18]. Superior to catalytic combustion which usually needs suitable conditions, it can operate at room temperature [19]. Moreover, compared with thermocatalysis,

photocatalysis is more effective for degradation of some recalcitrant organics, with few noxious intermediates but clean  $\text{H}_2\text{O}$  and  $\text{CO}_2$  left behind [14]. In practice, the catalyst temperature is actually elevated as most light sources supply consecutive UV–vis–IR irradiation. Therefore, integrating mild thermocatalysis into photocatalysis should be promising for utilizing idle IR energy, which is helpless in driving most photocatalysis because of the energy limit. However, IR-induced solar heating is generally repulsive in photocatalysis, as it usually leads to severe lattice vibration, damaging the photon-to-electron conversion [20]. Recently, we proposed a feasible strategy to address above IR-related contradiction, by integrating solid state ionics into photocatalysis [21]. Within fluorite  $\text{Ce}_{1-x}\text{Bi}_x\text{O}_{2-\delta}$  nanorods, the coupled electronic and ionic conduction help improve the negative temperature effect and integrate synergistic low temperature catalysis into solar energy utilization [21].

With photo/thermo-catalysis synergy, it has been proved that amazing enhancement can be achieved over  $\text{CeO}_2$ -based catalysts in VOCs abatement, such as formaldehyde [21] and benzene [22]. However, for practical application the low temperature performance needs to be further improved. On the other hand, for practical catalytic combustion the material sustainability is another key point. There have been reports that  $\text{Pt}/\text{TiO}_2$  shows better resistance to deactivation in photo/thermo-catalysis than in thermocatalysis alone [4,19]. However, the exact mechanism is still confusing and the cognition may be one-sided. It is worthwhile to explore the enhanced durability and in situ catalyst

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regeneration in photo/thermo-catalysis synergy, for better understanding the underlying mechanism and designing desired catalysts.

Inspired by previous reports, introducing various heteroatoms into fluorite ceria can help promote the spectral response as well as the oxygen mobility [23–30]. The enhancements stem from intricate factors, including energy band modulation, abundant vacancies and a more open crystal structure. Herein, through an alkali-modified approach,  $\text{Ce}_{1-x}\text{Mn}_x\text{O}_{2-\delta}$  solid solutions were prepared with moderate Mn contents ( $x < 0.4$ ). Incorporation of Mn into  $\text{CeO}_2$  helped improve the optical absorption and low temperature reducibility, simultaneously, inducing enhanced photo/thermo-catalysis synergy in the low temperature catalytic combustion of formaldehyde. Among the series of solid solutions,  $\text{Ce}_{0.75}\text{Mn}_{0.25}\text{O}_{2-\delta}$  with the nominal 3:1 Ce/Mn atom ratio presented the most excellent performance and was selected as the representative for detailed discussion. During prolonged dark reaction,  $\text{MnO}_x\text{-CeO}_2$  suffered gradual deactivation. However, the exhausted catalysts could be readily healed after in situ light irradiation, picking up more than 50% of the initial activity. In-depth discussions unveiled the mystique in the photo-induced self-remediation. Reductions of high valence metal ions as well as accumulation of noxious reaction intermediates and inert surface hydroxyls led to the catalyst deactivation. Fortunately, the in situ light irradiation could help recover the reduced  $\text{Mn}^{3+}$  ions and free the blocked active sites, inducing inspiring self-remediation. More generally, given the day and night alternations in nature, our results are instructive in designing reliable catalysts for efficient and sustainable catalytic combustion, such as the round-the-clock air purification.

## 2. Experimental

### 2.1. Chemicals and characterization

All the reagents were of analytical purity and used as received from Sinopharm Reagent Co. Ltd. without further purification. The purity and crystallinity of as-prepared catalyst powders were characterized by powder X-ray diffraction (XRD) with a Rigaku D/MAX 2250V diffractometer using monochromatized Cu  $K\alpha$  ( $\lambda = 0.15418$  nm) radiation under 40 kV and 100 mA. The crystal size was estimated from the Scherrer equation,  $D = (K\lambda)/(\text{FWHM} \cos \theta)$ , where  $D$  is the crystal size,  $\lambda$  is the wavelength of the X-ray radiation and  $K$  usually is taken as 0.89, FWHM is the full width at half maximum in radian of the sample. The morphologies and microstructures characterizations were performed on the transmission electron microscopy (TEM, JEOL JEM-2100F, accelerating voltage 200 kV). Energy dispersive X-ray spectrum (EDX) was collected from an attached Oxford Link ISIS energy dispersive spectrometer. Diffuse reflectance spectra were obtained on a UV-vis spectrophotometer (Hitachi U-3010) using  $\text{BaSO}_4$  as the reference. The  $\text{N}_2$ -sorption measurements were performed at 77 K using a Micromeritics Tristar 3000 analyzer. Temperature programmed reduction (TPR) was performed (for each sample, 40 mg) on a ChemiSorb 2750 instrument equipped with a thermal conductivity detector, under a 10%  $\text{H}_2/\text{Ar}$  flow ( $30 \text{ mL min}^{-1}$ ) at a heating rate of  $10^\circ\text{C min}^{-1}$ . Raman spectra were recorded with a ThermoFisher spectrometer (DXR) with an excitation length of 532 nm. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet iS10 FTIR spectrometer. X-Ray photoelectron spectroscopy (XPS) was employed to study the chemical states of the prepared samples. Spectra were performed on ESCALAB 250 (Thermo Scientific Ltd.) with a 320 mm diameter spot of monochromated aluminum  $K\alpha$  X-rays at 1486.6 eV under ultrahigh vacuum conditions. The C 1s signal was used to correct the charge effects.

### 2.2. Preparation of catalysts

$\text{MnO}_x\text{-CeO}_2$  ( $\text{Ce}_{0.75}\text{Mn}_{0.25}\text{O}_{2-\delta}$ , denoted as CeMn-A) was synthesized by a facile Alkali-modified hydrothermal process. In a typical procedure,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (3 mmol) and  $\text{KMnO}_4$  (1 mmol) were dissolved in deionized water (10 ml) and then mixed with a NaOH (6 M, 30 ml) solution. This mixture was kept stirring for 15 min with the formation of a milky suspension and then added into a 50 mL Teflon-lined autoclave with a stainless steel tank. The autoclave was finally subjected to the treatment at  $110^\circ\text{C}$  for 24 h. The precipitates obtained were rinsed with deionized water and anhydrous ethanol, and then freeze-dried and  $60^\circ\text{C}$  oven-dried in air successively. For comparison, pure  $\text{CeO}_2$  (denoted as Ce-A) was prepared by the same process without  $\text{KMnO}_4$  addition during the hydrothermal treatment.

### 2.3. Solar thermal measurement

100 mg powders of P25,  $\text{CeO}_2$  and  $\text{MnO}_x\text{-CeO}_2$  were dispersed in 6 ml anhydrous ethanol with the formation of suspension, respectively. Then, each suspension was dropwise and uniformly coated on a glass slide ( $25 \text{ mm} \times 76 \text{ mm}$ ). A 275 W tungsten filament lamp was used to drying the slides. During the solar thermal measurement, a Xe lamp ( $500 \text{ mW cm}^{-2}$ ) was used as the light source, simulating the sunlight. A contact thermocouple was used to record the temperature variation. A white hard casing was covered outside the thermocouple to avoid the solar heating effect over the thermocouple itself.

### 2.4. Catalytic degradation test

The catalytic activities of the two samples (100 mg) were evaluated by the gas-phase degradation of formaldehyde (250 ppm), operated in a gas-closed vitreous reactor (capacity 650 mL) with a quartz window and a double-walled jacket with circulating water for temperature control. A 500 W Xe lamp ( $500 \text{ mW cm}^{-2}$ ) and different temperatures were used to simulate various catalytic conditions. The degradation process was monitored by the increment of  $\text{CO}_2$  in the reactor by GC analysis (GC 7900, Techcomp) equipped with a TDX-01, 80–100 mesh packed column followed by a methane conversion furnace and a flame ionization detector (FID). It is worth noting that prior to any catalytic tests, the relevant condition must be maintained for several hours until the measured concentration of  $\text{CO}_2$  remained unchanged to obtain equilibrium between adsorption and desorption, eliminating all adventitious interference factors.

### 2.5. Electrochemical analysis

The electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell (quartz window, a working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) in saturated KCl as reference electrode). A Xe lamp (CHF-XM500) was used as light source equipped with various high-pass filters (400 nm, 450 nm and 510 nm) and positioned 6 cm away from the cell. To make a working electrode, as-obtained powders were deposited on a  $15 \times 25$  mm fluorine-doped tin oxide (FTO) substrate by nafion coating. Briefly, 10 mg of catalyst was suspended in 400  $\mu\text{L}$  of 1 wt% Nafion-ethanol solution and the mixtures were ultrasonically scattered for 15 min. Then, 150  $\mu\text{L}$  of supernatant homogeneous solution was dropped on the FTO glass. After evaporation of the ethanol, the catalyst attached FTO glass was used as the working electrode. The cyclic voltammetry (CV) curves were recorded from +1.0 to  $-0.5$  V vs. SCE, with a scanning rate of  $50 \text{ mV s}^{-1}$ . The current–time ( $i$ – $t$ ) curves were collected at

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