Introduce oxygen vacancies into CeO$_2$ catalyst for enhanced coke resistance during photothermocatalytic oxidation of typical VOCs

Jiejing Kong, Ziwei Xiang, Guiying Li, Taicheng An$^*$

Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Guangzhou Key Laboratory Environmental Catalysis and Pollution Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China

**ABSTRACT**

Carbon deposit during the catalytic oxidation of volatile organic compounds (VOCs) is a key factor to restrict long-term stability of catalysts. Herein, a modified ordered porous catalyst with high coke-resistance performance was developed by introducing oxygen vacancies (OVs) into CeO$_2$ through simple redox and steam treatment (ARCeO$_2$), and applied in efficiently photothermocatalytic degradation of VOCs. Abundant OVs in ARCeO$_2$ leads to enhanced light absorption, improved charge separation and increased reactive oxygen generation, and then promote its photothermocatalytic performance. Moreover, no obvious decrease was observed in the photothermocatalytic activity of ARCeO$_2$ at 200°C for 25 h reaction. Its superior photothermocatalytic stability can be attributed to the less intermediates and limited coke accumulation onto ARCeO$_2$. This work provides a facile and cost-effective strategy for the design and fabrication of CeO$_2$ catalyst with strong coke-resistance potential and highlights the significance of OVs engineering for improving the photothermocatalytic performance of VOCs degradation.

**Keywords:** Photothermocatalytic degradation, VOCs, ARCeO$_2$, Oxygen vacancy, Coke, Resistance

1. Introduction

Volatile organic compounds (VOCs), such as aromatic hydrocarbons straight-chain alkanes and cycloalkanes, are typical gaseous pollutants emitted from refinery and electronic waste dismantling processes, and then directly cause harm to human health and the environment [1,2]. Both photocatalytic oxidation and thermocatalysis reaction onto metal oxide catalysts are suggested to be the highly effective and economical techniques for VOCs removal [3–6]. However, most metal oxide catalysts suffer from low photocatalytic efficiency in the abatement of aromatics and alkane, because benzene ring and C–C bond are hard to be cracked [5]. For example, only 34.2 % of styrene [7] and 30 % n-hexane [8] can be degraded over TiO$_2$ in the continuous flow fixed bed reactor with full spectrum and UV illumination, respectively. Besides, high temperature (> 500 °C) is always required to effectively eliminate the saturated alkanes onto metal oxide catalysts (such as Fe$_2$O$_3$ [9]), leading to high energy costs. The development of metal oxide catalysts and the enhancement of their catalytic reaction processes for VOCs removal at low temperature is still a challengeable topic.

Ceria (CeO$_2$) with a band gap of $\sim 3.2$ eV has been widely investigated as a photo/thermocatalyst because of its superior properties, for instance, easy Ce$^{3+}$/Ce$^{4+}$ redox cycle, high oxygen mobility at moderate temperature, and high chemical/photochemical stability [10,11]. However, the accumulation of intermediates and even carbon deposits always inevitably occur during the catalytic processes, which would poison the active site of the catalyst for rapid decline in its catalytic activity [4,12]. The main reason of the formation of intermediates and coke deposits is that the inadequate generation of reactive oxygen species causes incomplete oxidation of VOC molecule instantly [13]. Recently, combining thermocatalysis with photocatalysis to maximize synergistic effects has been proven to be an effective method to promote the formation of more reactive oxygen species [14–17].

Primarily, the photothermocatalytic oxidation processes onto CeO$_2$ for VOC removal comply with Mars-van Krevelen mechanism [17], which can be summarized as follows: (1) the adsorbed VOCs molecules are oxidized with reactive oxygen species (such as O$_2^-$, O$^-$, h$^+$, 'OH and 'O$_2$•) generated onto CeO$_2$ by both thermal and photo excitation, along with the reduction of CeO$_2$ to produce CeO$_2$; (2) the reduced CeO$_2$ is re-oxidized to CeO$_2$ by gaseous O$_2$ and the reactive oxygen species generated under photoexcitation. It has been widely accepted that from the activating oxygen to reactive oxygen species is the rate-determining step, and oxygen vacancies (OVs) can not only act as an electron donor to effectively capture gaseous oxygen and strengthen the mobility of lattice oxygen [18,19], but also accelerate the separation and migration of photogenerated charge for facilitating the activation of oxygen [20]. Therefore, introduce OVs into CeO$_2$ can further

---

$^*$Corresponding author.
E-mail address: antic99@gdut.edu.cn (T. An).

https://doi.org/10.1016/j.apcatb.2020.118755
Received 6 January 2020; Received in revised form 8 February 2020; Accepted 11 February 2020
Available online 12 February 2020

0926-3373/ © 2020 Elsevier B.V. All rights reserved.
promote photothermocatalytic degradation efficiencies of VOCs. Crafting OVs can be usually realized by partial reduction of CeO2 into the non-stoichiometric form CeO2-x, with methods such as (1) thermal treatment at reductive atmosphere such as H2, CO, NH3, vacuum and NaBH4 (Reductant + O\text{Lattice} \rightarrow OVs + Oxidized reductant); (2) electrochemical reduction; and (3) photolysis by ultraviolet radiation (Light + O\text{Lattice} \rightarrow OV + 1/2O2) [21].

It is noted that OVs sites also serve as activated acid sites, where the imbalance of atomic electronegativity leads to a greatly increase in acidity and then improves the catalytic activity of bond breaking, polymerization and isomerization [22]. As a result, carbon deposits are prone to take place at OVs sites with their strong acidity during the catalytic oxidation process of VOCs. Much research has suggested that doped with alkali/alkali-earth metal or metal oxide [23], high-temperature calcination [24], steam pre-treatment [22] and pre-carbon-deposit treatment [25] could significantly reduce the catalyst surface acidity and amount of acid sites, but always accompanied by the decline of OVs. The trade-off between acidity and OVs in catalyst is a serious concern for its subsequent catalytic performance during the catalytic reaction processes.

Herein, in order to attain high catalytic activity and good stability performance for degradation of VOCs, a modified CeO2 ordered porous catalyst with high coke-resistance potential was developed and applied to the photothermocatalytic degradation of typical VOCs under simulated solar irradiation. The abundant OVs with weak acidity was introduced into modified CeO2 and further characterized by XPS, EPR, Raman and NH3-TPD. The results found that the catalytic activity of this newly prepared catalyst can effectively promote light harvesting, charge separation, reactive oxygen generation and reducibility, which then subsequently improved the photothermocatalytic degradation performance of VOCs. Characterization of intermediate accumulation and carbon deposit during the photothermocatalytic degradation of VOCs have also been conducted to understand the high performance as well as good stability onto this modified CeO2 ordered porous catalyst.

2. Experimental

2.1. Preparation of catalysts

CeO2 ordered porous catalyst was prepared by a colloidal crystal template method reported in our previous work [16], then treated under the three different conditions respectively: (I) Annealed it in the N2 atmosphere at 400 °C for 3 h, then turned the flow of air/N2 (volume ratio = 1:1) for another 2 h and then get obtained product which was denoted as CeO2; (II) Reduced it in the H2/N2 (volume ratio = 1:1) atmosphere at 400 °C for 2 h, then annealed it in N2 atmosphere at 400 °C for 1 h, followed by calcining in the air/N2 (volume ratio = 1:1) atmosphere at 400 °C for another 2 h to obtain the final product denoted as RCO2; (III) Reduced it in the humid H2/N2 (volume ratio = 1:1) atmosphere at 400 °C for 2 h (humid condition was achieved with N2 flow into the ultrapure water at 30 °C, relative humidity = 40 %), followed by annealing in the N2 atmosphere at 400 °C for 1 h, then calcined it in the air/N2 (volume ratio = 1:1) atmosphere at 400 °C for another 2 h, and the product obtained was denoted as ARGO2.

2.2. Catalysts characterisation

The morphology, structure, and composition of the materials were characterized by transmission electron microscopy (TEM, 200 kV, Talos-F200S, FEI), X-ray diffraction (XRD, DB ADVANCE, Bruker) and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher). The optical properties of the catalysts were measured on UV–vis spectrophotometer (DRS, Agilent Cary 300) and fluorescence spectrophotometer (PL, Fluorolog-3, HORIBA Instruments Incorporated) with a xenon lamp (excitation wavelength 280 nm) as light source. The electron paramagnetic resonance (EPR) tests were carried out in the X-band (9.84 GHz) with 4.00 G modulation amplitude and a magnetic field modulation of 100 kHz using a EPR spectrometer (EMXPlus-10/12, Bruker) at 77 K. Raman scattering measurements were recorded on a confocal Raman Spectroscopy (LabRAM HR Evolution, HORIBA Jobin Yvon), and the wavelength was set as 532 nm. Temperature-programmed reduction of H2 (H2-TPR), temperature-programmed oxidation of O2 (O2-TPD) and temperature-programmed desorption of NH3 (NH3-TPD) were investigated using TP-5078 Autochem-absorption analyzer, with approximately 20 mg of catalysts loaded in a quartz tube. Prior to each test for H2-TPR, the catalyst was pretreated under high-purity N2 at 30 °C for 1 h, then heated from 30 °C to 780 °C at 12 vol.% H2/N2 atmosphere with a flow rate of 30 mL min⁻¹ in the dark or under simulated solar irradiation. The illumination condition was achieved by equipping the furnace with a small window on its one side and 300 W Xe lamps on the outside. The consumption of H2 was detected using a thermal conductivity detector (TCD) (Xianquan Industrial and Trading Co., Ltd.). For O2-TPD experiment, 20 mg of the samples were pretreated at 30 °C for 1 h under high-purity Ar flow, then exposed to 40 vol.% O2/Ar with a flow rate of 30 mL min⁻¹. O2-TPD profile was recorded from 30 °C to 800 °C at a heating rate of 10 °C min⁻¹ and O2 consumption was measured using a TCD detector. Prior to each NH3-TPD run, the catalyst was pretreated under high-purity N2 at 90 °C for 1 h, then turned the flow of 10 vol.% NH3/N2 into the system with a flow rate of 30 mL min⁻¹ for 1 h. After that, the catalyst was flushed with high-purity N2 to remove physically adsorbed NH3 on the catalyst surface. Finally, the system was heated to 700 °C at a heating rate of 10 °C min⁻¹, and the NH3 desorption profiles were recorded under N2 flow by TCD detector.

2.3. Activity test

Photothermocatalytic degradation reactions were conducted in a tube (i.d. = 6 mm) fixed-bed reactor at atmospheric pressure, and the catalyst can be irradiated through a small window on the one side of the furnace, as schematized in Fig. S1 of Supporting Information. The simulated solar irradiation came from 300 W Xe lamp (λ ≈ 300 – 780 nm, optical power density is 200 mW cm⁻²). Approximately 0.1 g catalyst was packed in the reactor. The vapor of styrene, n-hexane or cyclohexane was generated by passing N2 at a certain flow rate through the corresponding solution (≥ 99 %), and the vapor was mixed with dry air to achieve different VOCs concentration. The final VOCs concentration of ~ 50 ppm was fixed in the feeding gas by controlling the solution temperature and N2 flow rate through a saturator. Gas hourly space velocity (GHSV) value of 30,000 mL h⁻¹ g⁻¹ was tested. The concentrations of VOCs and CO2 were respectively measured using the gas chromatograph GC-9800 (FID) and GC9800 (FID, equipped with a Ni catalyst based methanizer), and detail analysis process was given in Supporting Information. Three to five concentration data were measured at each temperature with around a 10 min interval. The concentration data adopted showed less than 10 % difference from other measured data at each temperature. The mineralization/degradation of VOCs was assessed by the following equations:

\[
\text{Styrene Degradation} = \frac{[C_8H_8]_{in} - [C_8H_8]_{out}}{[C_8H_8]_{in}} \times 100\%
\]

\[
\text{Styrene Mineralization} = \frac{[CO_2]_{out}}{[C_8H_8]_{in}} \times 100\%
\]

\[
n - \text{Hexane Degradation} = \frac{[C_{16}H_{34}]_{in} - [C_{16}H_{34}]_{out}}{[C_{16}H_{34}]_{in}} \times 100\%
\]

\[
\text{Cyclohexane Degradation} = \frac{[C_8H_8]_{in} - [C_8H_8]_{out}}{[C_8H_8]_{in}} \times 100\%
\]

where \([C_8H_8]_{in}, [C_8H_8]_{out}\) and \([C_8H_8]_{in}\) are the inlet molar quantity of...
vaporous styrene, n-hexane and cyclohexane, respectively; \([C_4H_8]_{\text{out}}, [C_6H_{14}]_{\text{out}}, [C_7H_{12}]_{\text{out}}\) and \([\text{CO}_2]_{\text{out}}\) are the outlet molar quantity of vaporous styrene, n-hexane, cyclohexane and \(\text{CO}_2\), respectively.

2.4. The identification of intermediates

The trace intermediates deposited onto the spent catalyst surface were extracted ultrasonically with 60 mL chromatographic grade methanol for 5 min and then stored overnight in the fridge (\(-18^\circ\text{C}\)). The extract was filtered through a 0.22 \(\mu\text{m}\) filter membrane and concentrated with a vacuum rotary evaporator, then completely dried with a gentle stream of high-purity \(\text{N}_2\). Afterwards re-dissolved it with 1.0 mL ethyl acetate and injected directly into a gas chromatography-mass spectrometer (GC-MS, Agilent 7890B-5977B) for the identification of intermediates, and detail analysis process was given in Supporting Information.

3. Results and discussion

3.1. Structural properties

\(\text{CeO}_2\), \(\text{R CeO}_2\) and \(\text{AR CeO}_2\) catalysts were obtained by the modification of raw \(\text{CeO}_2\), including directly calcination, redox calcination, redox calcination with steam treatment, respectively. As shown in Fig. 1a-c, TEM images of the three samples exhibit the ordered texture with macropores (120 nm) and uniformly sized walls interconnected with small windows. Besides, XRD patterns in Fig. 1d prove that \(\text{CeO}_2\), \(\text{R CeO}_2\) and \(\text{AR CeO}_2\) are all composed of cubic cerianite structure (JCPDS No. 34-0394). No significant difference has been observed in either TEM or XRD spectra for the three resultant catalysts, suggesting the similar morphology, crystal phase, crystallinity, and particle size of the three samples obtained under different atmosphere calcinations as described in the reference [26].

XPS experiment was conducted to explore the valence states of elements and the types of oxygen species over \(\text{CeO}_2\), \(\text{R CeO}_2\) and \(\text{AR CeO}_2\), as presented in Fig. 2a and b. For \(\text{Ce} 3d\) spectra of these samples (Fig. 2a), all of them are fitted by eight bands marked as \(\alpha_1\), \(\alpha_2\), \(\alpha_3\), \(\alpha_4\) and \(\beta_1\), \(\beta_2\), \(\beta_3\), \(\beta_4\). Moreover, the bands of \(\alpha_2\) and \(\beta_2\) are resulted from \(\text{Ce}^{3+}\) ions while the others are corresponded to \(\text{Ce}^{4+}\) species according to the references [15,16]. It is reported that a rise in \(\text{Ce}^{3+}\) favors the increase in the amount of the OVs and the relatively high mobility of the bulk oxygen species, then facilitates catalytic oxidation reaction [27]. It is generally accepted that the area ratio of \(\alpha_2 + \beta_2\) to the total eight bands can reflect \(\text{Ce}^{3+}\)/\(\text{Ce}^{4+}\) ratio on the surface of the samples [28]. Consequently, the relative amount of \(\text{Ce}^{3+}\) in the samples was estimated based on the above area ratio, and the results are listed in Table S1. The ratio of \(\text{Ce}^{3+}\) over these samples was in the order of \(\text{AR CeO}_2\) (21.7 %) > \(\text{R CeO}_2\) (20.6 %) > \(\text{CeO}_2\) (18.4 %). As the migration and transformation of oxygen species over catalysts are also important for the catalytic reaction, \(\text{O} 1s\) spectra of \(\text{CeO}_2\), \(\text{R CeO}_2\) and \(\text{AR CeO}_2\) have been investigated and are given in Fig. 2b. All the \(\text{O} 1s\) XPS spectra of these samples can be fitted into three Gaussian peaks at 531.7 and 529.2 eV, assigned to surface adsorbed oxygen species (\(\text{O}_\alpha\)) and lattice oxygen species (\(\text{O}_\beta\)), respectively [29,30]. As the migration ability of surface adsorbed oxygen species (including chemisorbed oxygen \(\text{O}^{2-}\), \(\text{O}^-\) and hydroxyl group) is remarkably stronger than that of lattice oxygen species, the adsorbed oxygen is viewed as the dominant reactive oxygen species and plays a dominant role in the redox reaction [31]. In other words, the ratio of \(\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)\) could reflect the content of reactive oxygen species of the reaction [30]. Table S1 shows that the \(\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)\) ratio has a sequence of \(\text{AR CeO}_2\) (31.4 %) > \(\text{R CeO}_2\) (28.6 %) > \(\text{CeO}_2\) (18.0 %). As the surface adsorbed oxygen species mainly exists on the defect sites (e.g., OVs) of catalysts, it can be suggested that the reduction of \(\text{Ce}^{4+}\) to \(\text{Ce}^{3+}\) in \(\text{AR CeO}_2\) after redox and steam treatment facilitates the formation of OVs, further promoting the oxygen escaping from the lattice sites and leaving vacant sites with two electrons at each vacancy, then generates more reactive oxygen.

To further analyze \(\text{Ce}\) species states and OVs in \(\text{CeO}_2\), \(\text{R CeO}_2\) and \(\text{AR CeO}_2\), EPR characterization was also performed and summarized in Fig. 2c. The signals marked by asterisks correspond to Mn\(^{2+}\) ion impurity, which is due to the quartz tube of EPR equipment [32]. The signal occurred at \(g = 2.002\) represents the superoxide anions (\(\text{O}_2^-\)) attached with the \(\text{Ce}^{4+}\) ions [16,32], and its intensity mainly associated with OVs concentration [33]. Besides, the \(g\) value of 1.963 corresponds to the \(\text{Ce}^{3+}\) species next to unpaired electrons (\(\text{O}_2^-\) and \(\text{O}^-\)) [32–34]. The intensity of \(\text{Ce}^{3+}\) and OVs were both in the order of \(\text{AR CeO}_2\) > \(\text{R CeO}_2\) > \(\text{CeO}_2\), demonstrating that the redox and steam treatment reduced \(\text{Ce}^{4+}\) to \(\text{Ce}^{3+}\) in the \(\text{CeO}_2\) lattice then generated more OVs.

Furthermore, Raman spectroscopy was performed to further verify the lattice defects of these samples, as shown in Fig. 2d. Over \(\text{CeO}_2\), the Raman spectra present a only characteristic peak at around 464 cm\(^{-1}\), corresponding to the \(\text{F}_2\)g vibration mode of octahedral local symmetry around cubic fluorite structure of \(\text{CeO}_2\) [33]. For \(\text{R CeO}_2\) and \(\text{AR CeO}_2\), two new Raman scattering peaks could be observed with a broad shoulder at 602 cm\(^{-1}\) and one weak band at 252 cm\(^{-1}\). Both peaks are ascribed to the defects-induced vibration mode, especially oxygen defects [28,33]. The difference in wavenumber between the oxygen defect (602 cm\(^{-1}\)) and \(\text{F}_2\)g bands (464 cm\(^{-1}\)) is \(\sim 140\) cm\(^{-1}\), suggesting that OVs of \(\text{R CeO}_2/\text{AR CeO}_2\) catalyst are generated from intrinsic defects \((\text{Ce}^{4+} \rightarrow \text{Ce}^{3+})\) [30]. It is generally considered that the intensity ratio between defects-induced vibration mode and \(\text{F}_2\)g mode (i.e., \(I_{602}/I_{464}\)) is proportional to the concentration of OVs in the \(\text{CeO}_2\)-based materials [35]. The value of \(I_{602}/I_{464}\) for \(\text{AR CeO}_2\) (ca. 0.1723) is slightly higher than that for \(\text{R CeO}_2\) catalyst (ca. 0.1571), while the characteristic peaks of OVs are absent over \(\text{CeO}_2\) due to its low OVs concentration. This phenomenon is consistent with XPS and EPR results above.

It is well known that the surface acidity of catalysts is not only an indispensable factor for carbon deposit, but also for catalytic performance of VOCs oxidation [36]. Thus, to characterize the catalyst surface acidity, the NH\(_3\)-TPD of these three catalysts was illustrated. As presented in Fig. 3, two NH\(_3\) desorption peaks were observed over all samples, with the peak appearing at low temperature (100–250 °C, \(\alpha\))...
peak) corresponded to the weak acid sites and the high temperature peak (> 300 °C, \( \beta \) peak) assigned to strong acid sites [29]. Compared with CeO_2, the \( \alpha \) peak of both RCeO_2 and ARCeO_2 shifted from 190 °C to 152 °C with stronger desorption intensity, indicating a decline of acid strength but increase of weak acid quantity. Besides, the desorption temperature of \( \beta \) peak over CeO_2, RCeO_2 and ARCeO_2 is 438 °C, 438 °C and 385 °C, respectively, and the latter two showed stronger signal than that of CeO_2. All these results reveal that both RCeO_2 and ARCeO_2 possess more acid sites than that of CeO_2. In comparison with RCeO_2, steam treatment for ARCeO_2 did not change the amount of strong acid sites but weaken its acidity, which may have positive effects on the adsorption of VOCs molecules [29,37], simultaneously enhanced coke resistance during photothermocatalytic oxidation of typical VOCs [38].

Based on the above results, we know that when CeO_2 ordered porous catalyst was modified by redox treatment, in which firstly reduced by calcination in H_2 atmosphere at 400 °C, OVs could be successfully introduced into CeO_2 catalyst (denoted as RCoO_2) by partial reduction of Ce^{4+} to Ce^{3+} [21,39]. The as-introduced OVs would induce a greatly increase in the surface acid sites of catalyst due to its imbalance of atomic electronegativity [22]. In this context, the rich OVs and abundant acid sites were observed on RCoO_2 (Figs. 2d and 3). It is reported that steam pre-treatment of catalyst could significantly reduce its acidity and amount of acid sites [22]. After modification of CeO_2 by combining redox process with steam treatment, surface acidity of the obtained catalyst (ARCeO_2) has weakened, as indicated by \( \text{NH}_3 \)-TPD profiles (Fig. 3). Moreover, as the modifying temperature (400 °C) is much lower than the preparation temperature (600 °C) of raw CeO_2, the morphology and crystal phase of ARCeO_2 show no observed change (Fig. 1c and d). Also, ARCeO_2 catalyst maintains the rich OVs, which is confirmed by XPS and Raman characterization (Fig. 2). All these phenomena imply that conducting the redox and steam treatment on simultaneously could successfully introduce OVs into CeO_2 catalyst and synchronously weaken its surface acidity, demonstrated the advantages of our modification method.

### 3.2. Catalytic performance

The influence of both OVs concentration and surface acidity of catalysts on its photothermocatalytic degradation activity of three typical VOCs (including styrene, n-hexane and cyclohexane) is investigated and compared in Fig. 4. As shown in Fig. 4a, the photothermocatalytic degradation of styrene under simulated solar irradiation without catalyst below 250 °C can be negligible, and the activity profiles demonstrate that the catalytic activity varies with both OVs concentration and acidity of catalysts. ARCeO_2 exhibited the best initial photocatalytic performance (30 °C) and highest thermocatalytic activity among the three samples (Figs. 4 and S2). When under photothermocatalytic conditions (> 30 °C), ARCeO_2 also demonstrates the best apparent performance with the 30 % styrene degradation temperature (T_{30}) at 43 °C, 50 % styrene degradation temperature (T_{50}) at 136 °C and 90 % styrene degradation temperature (T_{90}) at 226 °C (Fig. 4a and Table S2). Particularly, T_{30} of ARCeO_2 shows much lower than that of RCoO_2 (104 °C) and CeO_2 (160 °C). Moreover, compared with ARCeO_2 in the dark (T_{30,dark} at 176 °C, T_{50,dark} at 206 °C and T_{90,dark} at 245 °C), ARCeO_2 under simulated solar irradiation exhibited much more improved catalytic activity, especially at the low temperature region (T < 200 °C). It is noted that thermocatalytic activity of ARCeO_2 (11 % styrene degradation at 100 °C) in the low temperature is much weaker than the initial activity in photocatalysis (28 % styrene degradation at 30 °C), so it can be speculated that photocatalysis plays a
key role at a low reaction temperature (30 – 100 °C) of photothermocatalytic process (Fig. 4a). When in the relatively high temperature (150 – 200 °C), a photothermocatalytic synergistic performance of ARCeO₂ is demonstrated, which shows remarkably higher styrene degradation than the contribution addition from the pristine photocatalysis and thermocatalysis (Fig. 4a). Besides, by proper processing data in Fig. 4a according to the reference [16], the Arrhenius plots could be drawn and Eₐ values could be obtained for each sample from the slope of the Arrhenius plots, as presented in Fig. 4b. The estimated Eₐ value was around 15.6 kJ mol⁻¹ for ARCeO₂ under simulated solar irradiation, which was observably lower than those of ARCeO₂ in the dark (48.2 kJ mol⁻¹), RCeO₂ (20.9 kJ mol⁻¹) and CeO₂ (36.8 kJ mol⁻¹) under simulated solar irradiation. This result indicates that the redox and steam treatment, together with the existence of a photothermocatalytic synergetic effect onto ARCeO₂ can greatly decrease the activation energy of styrene oxidation. Lower activation energy remarkably reduces the reaction energy barrier and shows more conductive for the catalytic reaction to proceed smoothly [40].

To further explore the applicability of the as-developed catalyst with introduced OVs and surface acid sites, the photothermocatalytic degradation performance of ARCeO₂ for n-hexane and cyclohexane was also checked (Fig. 4c and d), and the comparison results of the three samples were summarized in Table S2. Obviously, among all the samples, ARCeO₂ also performs the highest apparent activity in photothermocatalytic degradation of both n-hexane and cyclohexane. The 20 % n-hexane degradation temperature of ARCeO₂ is obtained as 142 °C, showing 98 °C and 172 °C lower than that for RCeO₂ and CeO₂, respectively. Moreover, the 20 % cyclohexane degradation temperature of ARCeO₂ at 213 °C, also exhibits significantly lower than that of RCeO₂ (333 °C) and CeO₂ (432 °C). All these results reveal that OVs and surface acid sites in ARCeO₂ can greatly promote the photothermocatalytic degradation of various typical VOCs, such as benzene series, straight-chain alkane and cycloalkanes.

### 3.3. Photothermocatalytic mechanism of catalyst

To gain insight into the photothermocatalytic mechanism enhanced by ARCeO₂, its optical properties including light response and charge separation are evaluated and illustrated first in Fig. 5. All the samples exhibit similar UV–vis diffuse reflectance spectra (DRS) and the UV–vis absorption intensity ranked by ARCeO₂ > RCeO₂ > CeO₂ (Fig. 5a). It is widely accepted that OVs can largely modify the optical properties of metal oxides as the OVs-induced defect states are involved in new photoexcitation processes [41]. The higher OVs concentration in ARCeO₂ exhibited the stronger light absorption both in UV and visible-light region (Fig. 5a). Besides, two absorption bands at 241 and 320 nm
for all the three catalysts can be observed and were ascribed to charge transfer transitions: \( \text{O}_2^− \rightarrow \text{Ce}^{3+} \) and \( \text{O}_2^− \rightarrow \text{Ce}^{4+} \), respectively \([34]\). The main absorption edges of the three samples are around 430 nm and the corresponding optical band gaps \( (E_g) \) are estimated to be 2.9 eV. The valence band edges obtained from XPS valence band spectra of CeO2, RCeO2 and ARCeO2 are estimated to be ca. 2.5, 2.3 and 2.3 eV, respectively, implying that redox treatment slightly changed the valence band structure of CeO2 (Fig. S3). In combination with the estimated \( E_g \) values, their conduction band values are estimated to be ca. -0.4 for CeO2 and -0.6 eV for both RCeO2 and ARCeO2. The result reveals that OVs can elevate the conduction band position, and the more negative potentials of conduction band can supply a strong potential for adsorbed oxygen reduction to generate more reactive oxygen species, according to the reference \([6,42]\).

In addition, charge recombination was also analyzed by photoluminescence spectroscopy, as exhibited in Fig. 5b. ARCeO2 shows the weakest PL intensity, indicating that ARCeO2 has lower charge recombination but higher charge separation than that of CeO2 and RCeO2. Since the surface OVs can prevent the charge carrier from recombination by trapping the electrons via their defect states, while it is more beneficial for these charges to transfer to the reactants on the catalyst surface efficiently \([43,44]\), ARCeO2 with OVs-rich demonstrated the highest charge separation capability among the three catalysts, which would effectively promote the photothermal catalytic reaction.

It is reported that photothermal catalytic oxidation mechanism of VOCs over CeO2-based catalysts can be interpreted in terms of the Mars–van Krevelen reduction–oxidation pathway \([16]\), and \( \text{H}_2\text{-TPR} \) analysis is an ideal tool for measuring the reduction behavior of the catalysts \([45]\). In this study, the \( \text{H}_2\text{-TPR} \) profiles of the catalysts in the dark and under illumination (\( \lambda = 300 \sim 780 \text{ nm} \)) was performed and displayed in Fig. 6. CeO2 under illumination shows two broad peaks, one at 418 °C and another at 522 °C. The first one is related to the reduction of the surface capping oxygen species of CeO2, and the second is associated with the reduction of \( \text{Ce}^{4+} \) to \( \text{Ce}^{3+} \) ions in the outermost layers (surface lattice oxygen) \([27,45]\). On ARCeO2 and RCeO2 under illumination, both peaks shift to lower temperatures in comparison with CeO2. Moreover, compared with ARCeO2 in the dark, the second reduction peak of ARCeO2 under illumination shifted to lower temperature range, and the \( \text{H}_2 \) consumption of the first peak apparently increased. Overall, the reducibility and mobility of surface oxygen species are generally improved over ARCeO2 under illumination, since the enrichment of OVs and photoexcitation prompt the adsorption/migration of gaseous/lattice oxygen, and then accelerate the activation of gaseous/lattice oxygen \([20]\). As the catalytic oxidation process could be facilitated by the high reducibility and diffusion of surface gaseous/lattice oxygen, ARCeO2 under photothermal catalytic conditions gives better catalytic performance for the degradation of VOCs.

As mentioned above, the oxidation of VOCs over CeO2-based catalysts under photothermal catalytic conditions has been generally interpreted in terms of the Mars–van Krevelen mechanism. According to this mechanism, the first step involves the reduction of CeO2 with the adsorbed VOC molecules, in which the adsorbed VOCs are simultaneously oxidized with reactive oxygen species (such as \( \text{O}_2^− \), \( \text{O}^− \), \( \text{h}^+ \), \( \cdot \text{OH} \) and ‘\( \cdot \text{O}_2 \)’) generated onto CeO2 by both thermal and photo excitation, and partial CeO2 is reduced to CeO2-x. The second step is to oxidize the reduced CeO2-x to CeO2 by both gaseous O2 and the photogenerated reactive oxygen species. Thus, the reducibility of CeO2 and capacity of reactive oxygen species generation determine the photothermal catalytic activity of CeO2. As discussed above, OVs introduced into CeO2 catalyst can effectively promote the adsorption/migration of gaseous/lattice oxygen, leading to the generation of more reactive oxygen species and lower \( \text{H}_2\text{-TPR} \) temperature peak onto ARCeO2 as compared with that of CeO2 (Figs. 2b and 6). In addition, photoexcitation also improved the reducibility of ARCeO2, as indicated by \( \text{H}_2\text{-TPR} \) characterization (Fig. 6). Moreover, ARCeO2 shows the strongest capacity of UV–vis absorption and the lowest charge recombination among the three samples, as confirmed by DRS and PL spectra (Fig. 5). The redox treatment for ARCeO2 induces a significant negative shift of the conduction band to enhance the reductive potential, and then supply a strong potential adsorbed oxygen reduction \([42,46]\). Both the unique optical properties and band structure of ARCeO2 are conducive to the generation of reactive oxygen species under photoexcitation. All these aspects accelerate the Mars–van Krevelen redox cycle, then leading to the remarkable enhanced photothermal catalytic activity of ARCeO2.

### 3.4. Stability test of catalyst

In order to evaluate the stability of prepared catalysts, cyclic photocatalytic degradation stability test of styrene over CeO2, RCeO2 and ARCeO2 with the total reaction time of 25 h were first investigated (Fig. 7a–c). It showed that CeO2 was completely deactivated after the second cycle (Fig. 7a), while the deactivation rate of both RCeO2 and ARCeO2 was much slower, and it was even not completely deactivated in the fifth cycle (Fig. 7b and c). In addition, during the photothermal catalytic degradation process of styrene over ARCeO2, styrene mineralization efficiencies show apparently lower than the corresponding degradation efficiencies in the temperature range of 30 – 200 °C (Fig. 7d), implying that lots of intermediates even coke were formed at that stage. Therefore, the temperature of 200 °C was chosen for long-term stability tests of catalysts in the dark and under illumination. As shown in Fig. 7e, an obvious decrease in the catalytic activity was observed onto all the prepared samples after 25 h reaction in the dark. Besides, ARCeO2 exhibited superior stability under illumination, with initial styrene degradation efficiency of 86.6 % at 200 °C decesing slightly to 78.3 % after 25 h reaction, while styrene degradation efficiency at 200 °C decreased rapidly from 68.8 % over RCeO2 and 62.3 % over CeO2 to 44.3 % and 30.4 % respectively under the identical reaction conditions (Fig. 7f). Results obtained suggest that the introduction of OVs and weak acidity onto ARCeO2, together with the synergic effect of photothermal catalysis promotes catalyst more resistant to deactivation.

### 3.5. Intermediates identification and coke resistance

To understand progressive deactivation of catalysts, the intermediates and carbon accumulation on catalyst surface were explored during photocatalytic (PC), thermocatalytic (TC) and photothermal catalytic (PTC) processes by temperature-programmed oxidation (TPO), GC–MS and XPS analysis. For simplification, the spent catalysts (CeO2, RCeO2 and ARCeO2) after cyclic stability test of PC degradation of styrene with the total reaction time of 25 h, long-term stability tests of TC and PTC degradation of styrene at 200 °C for 25 h, are respectively denoted as catalyst-PC (CeO2-PC, RCeO2-PC, ARCeO2-PC),
The TPO signals of all the above spent catalysts indicated three types of carbon-containing species deposited onto the catalyst surface: type I at 30–150 °C, type II at 150–250 °C and type III at 250–400 °C (Fig. 8a–c). Carbon-I represents non-volatile organic intermediates [47], while carbon-II and carbon-III were respectively assigned to amorphous and soft coke, which have a much lower combustion temperature than the polymeric or hard coke with high ratio of C/H [25,48]. All of the spent catalysts except ARCeO2-PTC showed apparent signals of carbon-I, indicating that parts of non-volatile intermediates could be easily accumulated onto catalyst surface during the PC, TC and even PTC processes. GC–MS analysis is also further applied to qualitatively identify these intermediates on the spent catalysts surface, and the corresponding results are all summarized in Table S3. It shows that the intermediates deposited onto CeO2-PC are all the O-containing benzene series, including benzaldehyde, phenol, benzyl alcohol, 2-phenoxymethane, 2,2-dihydroxy-1-phenylethan-1-one, benzoic acid, 2-hydroxy-1-phenylethan-1-one, 1-phenylethane-1,2-diol, and phenylethyl alcohol. Moreover, the species number of intermediates ranked by CeO2-PC (9) > RCeO2-PC (7) > ARCeO2-PC (5) and CeO2-PTC (5) > CeO2-TC (4) > RCeO2-TC (3) and ARCeO2-TC (3) > RCeO2-PTC (2) > ARCeO2-PTC (0), further demonstrating that little intermediates have been accumulated onto ARCeO2-PTC. Besides, a small amount of carbon-II (amorphous coke) but no carbon-III (soft coke) could be detectable over CeO2-TC, R CeO2-TC and ARCeO2-TC. Moreover, the peak intensity of carbon-III (soft coke) over CeO2-PTC, R CeO2-PTC and ARCeO2-PTC showed obviously weaker than that of the corresponding catalysts after 25 h photocatalytic stability test (CeO2-PC, R CeO2-PC and ARCeO2-PC), confirming the enhanced coke-resistance in photothermocatalysis, and it is observed that the signal intensity of carbon-III (soft coke) over CeO2-PTC, R CeO2-PTC and ARCeO2-PTC followed the sequence of R CeO2-PTC > CeO2-PTC > ARCeO2-PTC, indicating the highest coke resistance of ARCeO2. Finally, the coke resistance of CeO2, R CeO2 and ARCeO2 was semi-quantitatively compared by the C1s XPS spectra. As shown in Fig. 9, the spent catalysts (CeO2-PC, R CeO2-PC, ARCeO2-PC, ARCeO2-TC and ARCeO2-PTC) have the same composition of peaks, which includes three peaks at 284.8, 285.9, and 289.1 eV, attributed to sp2C (C-C, C = C), sp3 C (C-O), and oxidized C (C = O), respectively [49], and the content of assigned C1s is summarized in Table S4. For the PC process (Fig. 9a), the total content of carbon species on the samples was in the order of R CeO2-PC (39.4 %) > CeO2-PC (37.8 %) > ARCeO2-PC (32.0 %). Moreover, C-C/C = C species have the same sequence of R CeO2-PC (27.8 %) > CeO2-PC (25.9 %) > ARCeO2-PC (20.4 %). Higher C-C/ C = C concentration reflects more coke accumulation on the surface of the samples [16], suggesting that the rate of carbon deposit ranked by R CeO2 > CeO2 > ARCeO2 during the PC process. This result is consistent with TPO analysis in Fig. 8a. Besides, both the content of total
carbon species and C-C/C = C species of ARCeO2-PTC is slightly higher than that for ARCeO2-TC (Fig. 9b and Table S4).

3.6. Discussion on the enhanced photothermocatalytic stability of ARCeO2

As mentioned above, there is more coke accumulating onto RCeO2-PTC compared with CeO2-PTC (Fig. 8c), but RCeO2 still had better activity and stability in photothermocatalytic degradation of styrene than CeO2 (Figs. 4 and 7f). This phenomenon further confirmed the promotion effect of OVs on photothermocatalytic degradation of VOCs. Since OVs in catalyst lead to enhanced light absorption, improved charge separation and increased reactive oxygen generation (Figs. 5 and 6), and then promote the photothermocatalytic oxidation reaction (Fig. 4), the trade-off between high OVs concentration and high carbon deposit rate of RCeO2 results in the slower deactivation rate than CeO2. As ARCeO2 has more OVs than RCeO2 (Fig. 2), and the low surface acidity of ARCeO2 induces its enhanced coke-resistance performance (Figs. 8 and 9a), ARCeO2 proves the best long-term photothermocatalytic stability for VOC degradation among the three catalysts.

In addition, the coke amount of ARCeO2-PTC is slightly higher than that for ARCeO2-TC (Fig. 9b), while the stability of ARCeO2 in photothermocatalysis is better than that in thermocatalysis. This phenomenon implies that carbon deposit is not the cause of reduced thermocatalytic activity but the produced intermediates, and a little carbon deposit has ignorable negative impact on photothermocatalytic stability. Maybe it could be believed that though a small amount of coke on ARCeO2 surface would block a small part of its active sites, the increased light absorption and enhanced heat storage/release of coke (which can be seen as carbon-based material) could synchronously facilitate photothermocatalytic reaction, therefore prevent the rapidly deactivation of ARCeO2. Given the above, the synergistic effect of the abundant OVs and low surface acidity of ARCeO2, together with photothermocatalysis facilitated the oxidation of intermediates, and thus intensify coke resistance for high photothermocatalytic

4. Conclusions

ARCeO2 ordered porous catalyst with rich OVs and low surface acidity was successfully developed by simple redox and steam treatment. ARCeO2 exhibits substantially higher photothermocatalytic degradation performance in typical VOCs such as styrene, n-hexane and cyclohexane as compared with the directly calcined sample (CeO2) and the redox-treated sample (RCeO2), which is believed to due to enhanced light absorption, improved charge separation and increased reactive oxygen generation by OVs introduction. Additionally, the abundant OVs and weak acidity of ARCeO2, together with synergetic effect of photothermocatalysis facilitated the oxidation of intermediates, and thus intensify coke resistance for high photothermocatalytic
performance stability without any activity decline after 25 h reaction. This study proves that combine introducing OVs with reducing acidity is a feasible approach to achieve highly efficient simulated solar driven photothermalcatalysts with high coke-resistance potential.

CRediT authorship contribution statement

Jiejing Kong: Methodology, Writing - original draft. Ziwei Xiang: Data curation. Guiying Li: Writing - review & editing. Taicheng An: Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by Key-Area Research and Development Program of Guangdong Province (2019B110206002), National Natural Science Foundation of China (41731279 and 41415025), Local Innovative and Research Teams Project of Science Foundation Funded Project (2018M630925), Technical and Innovation Talents of Guangdong special support program (2016TX032094) as well as China Postdoctoral Science Foundation Funded Project (2018M630925).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2020.118755.