Removing Surface Hydroxyl Groups of Ce-Modified MnO₂ To Significantly Improve Its Stability for Gaseous Ozone Decomposition

Yang Liu†,‡ and Pengyi Zhang*,†,‡,§

†State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, and ‡Laboratory of Solid Waste Management and Environment Safety (Tsinghua University), Ministry of Education, Tsinghua University, Beijing 100084, China
§Beijing Key Laboratory for Indoor Air Quality Evaluation and Control, Beijing 100084, China

Supporting Information

ABSTRACT: Stratospheric ozone (O₃), which slips into the cabin through the air-supply system in a commercial airliner, is detrimental to human health around the world. For gaseous O₃ abatement, catalytic decomposition is an effective method. However, catalyst deactivation is one of the main obstacles to its practical application. In this study, a new deactivation mechanism involving the surface hydroxyl group of catalyst is found by investigating the effects of heat treatment of cerium-modified todorokite-type manganese dioxides (Ce-MnO₂) on O₃ decomposition, which will contribute to the development of more active and stable O₃ decomposition catalysts in the future work. The in situ DRIFT study indicates that gaseous O₃ reacted with surface hydroxyl groups to form surface adsorbed water, which occupied the catalytically active sites (i.e., oxygen vacancies) leading to the catalyst deactivation. Calcination at 300 °C greatly removed surface hydroxyl groups while keeping oxygen vacancies almost unchanged at the same time; thus the as-obtained catalyst showed greatly improved stability, keeping ~98% of removal efficiency for ~115 ppm of O₃ within 5 h under a very high space velocity of 1200 L g⁻¹ h⁻¹ at room temperature.

1. INTRODUCTION

Because of the growth of aviation transport in recent decades, it is essential to consider the air quality inside the cabin to ensure a comfortable and healthy journey. During a flight, the total air supply is a mixture of outside air and filtered recirculated air. Therefore, the stratospheric ozone (O₃) will slip into the cabin through the air-supply system in a commercial airliner. O₃ pollution is detrimental to human health, as reported by U.S., European, and Asian scientists in recent publications. Besides, the chemical interactions between gaseous O₃ and organic molecules inside the cabin may produce fine particles with adverse health effects.

Among various techniques, catalytic decomposition has been widely accepted as an effective method for gaseous O₃ removal at low temperatures. Transitional metal oxides are usually used for gaseous O₃ decomposition, such as Ag, Ni, Co, Ce, Cu, and Mn, etc. MnO₂ catalysts are very active for O₃ decomposition and are frequently used in gaseous O₃ removal. However, catalyst deactivation is one of the main obstacles to the practical application of the catalytic decomposition technique. Therefore, it is important to elucidate the underlying deactivation mechanism of the catalyst, which can help to improve the catalyst preparation and regeneration methods and finally prolong the lifetime of the catalyst. Up to now, Li and co-workers used in situ Raman spectroscopy and isotopic substitution to investigate the O₃ decomposition reaction. They found an adsorbed peroxide species acting as the reaction intermediate and that the desorption of these adsorbed intermediates regenerated the occupied active sites. Moreover, as was recently reported by Jia et al., O₃ decomposition usually proceeds through an oxygen vacancy (Vₒ)-involved mechanism, which can be simply described by the following three steps:

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\[ [O_3]_g + [V_{O_2}]_s \rightarrow [O-O_{V_2}]_s + [O_2]_g \]  

(1)

\[ [O_3]_g + [O-O_{V_2}]_s \rightarrow [O_2-O_{V_2}]_s + [O_2]_g \]  

(2)

\[ [O_2-O_{V_2}]_s \rightarrow [O_2]_g + [V_{O_2}]_s \]  

(3)

According to the above discussion, O\(_3\) decomposition stability greatly depends on the further transformation of the peroxyde-occupied oxygen vacancies \([O_2-O_{V_2}]_s\), if the decomposition of \([O_2-O_{V_2}]_s\), eq 3 is not sufficiently fast, the recovery of occupied oxygen vacancies will be hindered, thus resulting in catalyst deactivation.

Todorokite-type MnO\(_2\)_\(_\alpha\), consisting of triple chains of edge-sharing MnO\(_6\) octahedra, has a tunnel size of 0.69 nm. Because of its special structure and abundance in nature, the catalytic removal of gaseous O\(_3\) over todorokite-type MnO\(_2\) is of great significance and interest to scientific research and practical application. In our previous research, cerium modification greatly improved the O\(_3\) decomposition performance of todorokite-type MnO\(_2\).

Taking the very low humidity at high altitude into account, gaseous O\(_3\) decomposition under dry condition was carried out in this study, and a new deactivation mechanism for gaseous O\(_3\) decomposition involving surface hydroxyl groups was found by investigating the effects of heat treatment of cerium-modified todorokite-type MnO\(_2\) on gaseous O\(_3\) decomposition. The catalysts were characterized by various techniques, and the O\(_3\) decomposition reaction was in situ studied by infrared spectrometer. This work will deepen the understanding of catalyst deactivation and will contribute to the development of a highly active and stable O\(_3\) decomposition catalyst for practical application in commercial airliners.

### 2. EXPERIMENTAL SECTION

#### 2.1. Catalyst Preparation.

The Ce-modified todorokite-type MnO\(_2\) (Ce–MnO\(_2\)) was prepared according to the previous study. Briefly, it included three steps: synthesis of birnessite MnO\(_2\), ion exchange with Mg(CH\(_3\)COO)\(_2\) solution, and hydrothermal treatment of the ion-exchange product. The atomic ratio of Ce to Mn was kept around 0.28, which exhibited the best O\(_3\) decomposition performance in previous study. After the hydrothermal treatment, the resultant solid product was filtered, washed with deionized water three times, and dried at 105 °C overnight in an oven.

For post heat treatment, the pristine powder was calcined in air in an oven at desired temperatures for 3 h with a heating rate of 5 °C min\(^{-1}\) and then naturally cooled to room temperature. To make sure that the catalytic performances of different catalysts are comparable and reduce the gas flow resistance, the obtained powders were ground, shaped into tablets, then crushed and sieved to 40–60 mesh. For convenience, the samples calcined at 200, 300, and 400 °C were denoted as Ce–MnO\(_2\)(200), Ce–MnO\(_2\)(300), and Ce–MnO\(_2\)(400), respectively.

\(\alpha\)-MnO\(_2\) is generally considered as a kind of very active material for O\(_3\) removal; therefore, \(\alpha\)-MnO\(_2\) was prepared and compared to the Ce–MnO\(_2\) catalyst in this study. For the preparation of \(\alpha\)-MnO\(_2\), 40 mL of 0.2 M KNtMnO\(_2\) solution was added dropwise into 90 mL of 0.22 M Mn(CH\(_3\)COO)\(_2\) solution under vigorous stirring, and dark precipitates were formed. This suspension was aged at room temperature for 2 days, then filtered and washed with deionized water six times. The resultant solid product was dried at 105 °C in an oven overnight.

#### 2.2. Catalyst Characterization.

The changes of catalyst surface species with calcination temperature were observed with an in situ diffuse reflectance infrared Fourier-transformed spectrometer (in situ DRIFT, Nicolet 6700, Thermo Fisher, U.S.). To omit the unwanted peaks and make the comparison more obvious, the background was recorded with the pristine Ce–MnO\(_2\) in 50 mL min\(^{-1}\) of synthetic air (80 vol % of N\(_2\) and 20 vol % of O\(_2\)) at room temperature. The Ce–MnO\(_2\) powder was heated at a desired temperature for 3 h in 50 mL min\(^{-1}\) of synthetic air, and cooled to room temperature in the same atmosphere afterward. The spectra were acquired by averaging 32 scans at a resolution of 4 cm\(^{-1}\) in 50 mL min\(^{-1}\) of synthetic air at room temperature. After that, the sample was heated to the next temperature, and so on.

The thermal analysis was carried out on a thermogravimetric analyzer (TGA/DSC 1 STARe, Mettler Toledo, Switzerland). ~20 mg of the pristine Ce–MnO\(_2\) was heated to 800 °C in 20 mL min\(^{-1}\) of synthetic air with a heating rate of 5 °C min\(^{-1}\).

The crystal structures were examined on a Bruker D8-Advance X-ray diffractometer.

Raman spectra were acquired on a Renishaw inVia Raman microscope. The excitation source with a wavelength of 532 nm was used. Unless otherwise stated, the laser power was fixed at 2.5 mW. About 50 mg of catalyst powder was pressed into thin wafer and mounted onto the sample holder for observation.

The particle morphology was observed with scanning electron microscopy (SEM, S-5500, Hitachi, Japan) and transmission electron microscopy (TEM, JEOL-2100, Japan). The lattice images were taken using high-resolution TEM (HRTEM).

The specific surface areas of the samples were measured by the N\(_2\) adsorption BET method at ~196 °C (Autosorb-1, Quantachrome, U.S.). The samples were first degassed at 105 °C for 4 h before measurements.

The chemical states of the catalyst surface elements were examined by X-ray photoelectron spectroscopy (XPS, ESCA-LAB 250Xi, Thermo Fisher, U.S.). The reference energy used for calibration was the C 1s signal at 284.6 eV.

Temperature-programmed H\(_2\) reduction (H\(_2\)-TPR) experiments were carried out on a Chemisorption Analyzer (Autochem II 2920, Micromeritics, U.S.). About 50 mg of catalyst was used and pretreated in 50 mL min\(^{-1}\) of helium stream at 105 °C for 30 min. The catalyst was reduced in 5 vol % H\(_2\) in Ar with a flow rate of 50 mL min\(^{-1}\). The temperature was increased to 600 °C with a heating rate of 5 °C min\(^{-1}\). An isopropyl alcohol/liquid nitrogen slurry was used to maintain the temperature of cold trap at ~−80 °C. When the gas flow passed through the cold trap, the formed water from reduction could be removed before the gas flowed into the thermal conductivity detector (TCD). Therefore, the disturbance from water could be eliminated.

#### 2.3. O\(_3\) Decomposition Tests.

Catalytic decomposition of O\(_3\) was measured in a quartz tube reactor (i.d. 6 mm). Unless otherwise stated, the reaction conditions were as follows. ~50 mg of catalyst was loaded and kept around 25 °C in a water-circulated thermostat. A low-pressure mercury ultraviolet lamp (10 W, Guangdong Cnlight technology company, China) was used to generate O\(_3\) from pure O\(_2\) (purity >99.999%), and the O\(_3\) concentration was monitored online by an O\(_3\) analyzer (model 49h, Thermo Scientific, U.S.). A feed gas with a total flow rate of 1 L min\(^{-1}\) and 110–120 ppm of O\(_3\) was flowed.

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through the catalyst bed, corresponding to a space velocity of 1200 L g$^{-1}$ h$^{-1}$. O$_3$ conversion was defined as the ratio of the difference between inlet and outlet O$_3$ concentrations to the inlet O$_3$ concentration.

2.4. In Situ DRIFT Study of O$_3$ Decomposition. First, the Ce–MnO$_2$ powder was placed in the IR cell, and the background spectrum was recorded in 50 mL min$^{-1}$ of O$_2$ stream at room temperature. After that, the O$_3$ generator was switched on, and 50 mL min$^{-1}$ of O$_3$/O$_2$ stream with 105 ppm of O$_3$ was led into the IR cell. The time-resolved spectra were then obtained by averaging 32 scans at a resolution of 4 cm$^{-1}$ at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization Studies. 3.1.1. Changes of Adsorbed H$_2$O and Hydroxyl Groups by Heat Treatment. The changes of adsorbed H$_2$O and hydroxyl groups with calcination temperature were observed by in situ DRIFT, and the characteristic IR ranges for adsorbed H$_2$O and hydroxyl groups are displayed in Figure 1. As compared to the pristine Ce–MnO$_2$, there was no significant difference in Mn–OH (1273 cm$^{-1}$) after calcination at 200 °C for 3 h (Ce–MnO$_2$(200)). However, adsorbed H$_2$O apparently decreased over Ce–MnO$_2$(200). On the contrary, calcination at 300 °C for 3 h resulted in a dramatic loss of hydroxyl groups besides loss of water. Further decrease in adsorbed H$_2$O and hydroxyl groups was observed over the Ce–MnO$_2$(400) sample.

3.1.2. Thermal Analysis. Thermal analysis was performed over the pristine Ce–MnO$_2$ sample (Figure 2). The catalyst gradually lost its weight with increasing temperature. Six stages of weight loss could be distinguished from the DTG curve. The weight loss below 180 °C is ascribed to the desorption of physically adsorbed H$_2$O, and the chemically adsorbed H$_2$O began to desorb from the catalyst when the temperature was increased to 180 °C, from which it is reasonable to infer that the H$_2$O desorption observed at 200 °C in Figure 1 is due to the desorption of both physically and chemically adsorbed H$_2$O. The dehydration of hydroxyl groups usually occurred around 300 °C, which is also supported by the in situ DRIFT results in Figure 1. The weight loss peaks at 450, 510, and 560 °C could be attributed to the stepwise desorption of lattice oxygen species.

3.1.3. Crystal Structure. The XRD patterns of all four samples are shown in Figure 3A. For the pristine Ce–MnO$_2$, the typical diffraction peaks for todorokite-type MnO$_2$ (i.e., Mn–OH (1273 cm$^{-1}$) after calcination at 200 °C for 3 h (Ce–MnO$_2$(200)). However, adsorbed H$_2$O apparently decreased over Ce–MnO$_2$(200). On the contrary, calcination at 300 °C for 3 h resulted in a dramatic loss of hydroxyl groups besides loss of water. Further decrease in adsorbed H$_2$O and hydroxyl groups was observed over the Ce–MnO$_2$(400) sample.

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9.3°, 18.6°, and 37.3°) were observed. It is reported in the literature that the appearance of the diffraction peak at ~18.6° implies the formation of 3 × 3 tunnel structure. However, it can be clearly seen that calcination at 200 °C (Ce−MnO2(200)) substantially reduced the todorokite peaks, from which it can be deduced that the 3 × 3 tunnel structure was greatly weakened over Ce−MnO2(200), not to mention the Ce−MnO2(300) and Ce−MnO2(400) samples. It is generally accepted that H2O molecules and some metal ions (Mg2+, K+, etc.) exist in the todorokite tunnel, which play a supporting role in maintaining the tunnel structure, and the loss of these supporters is very likely to lead to the shrinkage of the 3 × 3 tunnel. Combined with the respective IR and thermal analysis results in sections 3.1.1 and 3.1.2, the XRD characterization suggests that heat treatment at 200 °C for 3 h could remove most of the tunnel H2O over Ce−MnO2. Moreover, the diffraction peaks around 19° were slightly shifted toward higher angles with the increase of calcination temperature, as shown in the step-scan patterns (inset view in Figure 3A), providing further evidence that the tunnel structure shrunk with the removal of tunnel H2O molecules.

Figure 4. SEM and (HR)TEM images of the samples: (A,B) pristine Ce−MnO2, (C,D) Ce−MnO2(200), (E,F) Ce−MnO2(300), and (G,H) Ce−MnO2(400). The areas marked with red boxes in the TEM images were used for HRTEM observations.
cm$^{-1}$ was observed over Ce–MnO$_2$(200), Ce–MnO$_2$(300), and Ce–MnO$_2$(400). As reported in the literature, strong laser power might cause decomposition of MnO$_2$ to Mn$_3$O$_4$, resulting in the appearance of strong Raman band at $\sim$650 cm$^{-1}$. Therefore, it is necessary to check whether the difference in Raman spectra is due to the destruction of the structure caused by laser irradiation. From the inset of Figure 3B, the peak profile and position of Ce–MnO$_2$(300) remained unchanged after the laser power was reduced to 0.25 mW (one-tenth of the laser power used in Figure 3B), which indicates that the laser-induced structural damage could be excluded in this study. Also, the significant change of the Raman spectra of Ce–MnO$_2$ after calcination is very likely to be due to the removal of H$_2$O, and this deduction is supported by the literature. The results of Raman characterization are consistent with the XRD data (Figure 3A), which indicates that the removal of H$_2$O by heat treatment will cause a great impact on the catalyst structure.

3.1.4. Morphological Changes and the Exposed Facets. Figure 4 illustrates the SEM and TEM images of the samples. The pristine Ce–MnO$_2$ mainly existed in sheets and belts (Figure 4A), which were transformed into stacked short rods with a small fraction of tiny sheets after being heated at 200 °C for 3 h (Ce–MnO$_2$(200), Figure 4C). Additionally, small pieces of bulk dominated over Ce–MnO$_2$(300), as shown in Figure 4E. Also, it can be seen from Figure 4G that 400 °C calcination would cause a certain degree of sintering, leading to a relatively smaller BET specific surface area ($S_{\text{BET}}$) of Ce–MnO$_2$(400). The $S_{\text{BET}}$ values for the pristine Ce–MnO$_2$, Ce–MnO$_2$(200), Ce–MnO$_2$(300), and Ce–MnO$_2$(400) were 108, 114, 103, and 86 m$^2$ g$^{-1}$, respectively.

Figure 4B, D, F, and H shows the TEM images of the samples, and the areas marked with red boxes were used for HRTEM observations, which are displayed in the insets correspondingly. All of the samples exposed the (111) facet of CeO$_2$, as indicated by the lattice spacing of 0.31 nm. Besides, the (004) facet of todorokite-type MnO$_2$ was found over the pristine sample (Figure 4B), Ce–MnO$_2$(200) (Figure 4D), and Ce–MnO$_2$(300) (Figure 4F). In addition to the (004) facet of todorokite-type MnO$_2$, Ce–MnO$_2$(400) (Figure 4H) exposed a new lattice spacing of 0.215 nm, which, however, does not belong to any of the crystal facets of todorokite-type MnO$_2$. As reported by Gao et al., the formation of a layered birnessite-type MnO$_2$ was observed by calcining α-MnO$_2$ (2 $\times$ 2 tunnel structure) at high temperature, indicating the possible transformation of the tunnel structure to layered structure. Moreover, according to the standard XRD pattern of birnessite MnO$_2$ (JCPDS no. 43-1456) and the literature, the lattice fringe of (112) facet of birnessite MnO$_2$ is 0.215 nm. Therefore, the lattice spacing of 0.215 nm observed over Ce–MnO$_2$(400) (Figure 4H) can be ascribed to the (112) facet of birnessite-type MnO$_2$.

3.1.5. Chemical States of Surface Elements. XPS analysis was used to examine the composition and chemical states of surface elements. The corresponding results are reproduced in Figure 5. The Mn 2p spectra (Figure 5A) can be deconvoluted into two pairs of peaks, and the binding energies of Mn 2p$_{3/2}$ at 641.1 and 642.3 eV with their corresponding Mn 2p$_{1/2}$ at 652.5 and 653.7 eV are assigned to Mn$^{3+}$ and Mn$^{4+}$, respectively. As reported in the literature, the lattice spacing of 0.215 nm, which, however, does not belong to any of the crystal facets of todorokite-type MnO$_2$. As reported by Gao et al., the formation of a layered birnessite-type MnO$_2$ was observed by calcining α-MnO$_2$ (2 $\times$ 2 tunnel structure) at high temperature, indicating the possible transformation of the tunnel structure to layered structure. Moreover, according to the standard XRD pattern of birnessite MnO$_2$ (JCPDS no. 43-1456) and the literature, the lattice fringe of (112) facet of birnessite MnO$_2$ is 0.215 nm. Therefore, the lattice spacing of 0.215 nm observed over Ce–MnO$_2$(400) (Figure 4H) can be ascribed to the (112) facet of birnessite-type MnO$_2$.

Figure 5. (A) Mn 2p, (B) O 1s, and (C) Ce 3d XPS spectra of the samples: (a) pristine Ce–MnO$_2$, (b) Ce–MnO$_2$(200), (c) Ce–MnO$_2$(300), and (d) Ce–MnO$_2$(400).

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changes of Mn$^{3+}$/Mn$^{4+}$ and O$_{2u}$/(O$_{1}$+O$_{2u}$+O$_{3u}$) ratios with calcination temperature are illustrated in Figure 6. When the
calcination temperature was lower than 300 °C, the Mn$^{3+}$/Mn$^{4+}$ ratios decreased very slowly with increasing calcination temperature, while further increasing calcination temperature to 400 °C resulted in a rapid decrease in the Mn$^{3+}$/Mn$^{4+}$ ratio. On the basis of the principle of electroneutrality, a higher Mn$^{3+}$/Mn$^{4+}$ ratio indicates more oxygen vacancies (i.e., catalytically active sites for O$_3$ decomposition). Therefore, it is reasonable to infer that the change of oxygen vacancy with calcination temperature should show the same trend as that of the Mn$^{3+}$/Mn$^{4+}$ ratio. As shown in Figure 6 for the O$_{2u}$/(O$_{1}$+O$_{2u}$+O$_{3u}$) ratios, there was no observable difference between the pristine Ce–MnO$_2$ and Ce–MnO$_2$(200), while a significant decrease of surface hydroxyl group over Ce–MnO$_2$(300) was observed, which is in accordance with the in situ DRIFT (Figure 1) and thermal analysis (Figure 2) results. In addition, the Ce$^{3+}$/Ce$^{4+}$ ratios were in the range of 8%–12%, which implies the dominance of Ce$^{3+}$ in all samples.

3.1.6. Redox Behavior of the Samples. H$_2$-TPR results are displayed in Figure 7. Two reduction peaks were detected over all samples. On the basis of the XPS results of Mn 2p (Figure 5A) and Ce 3d (Figure 5C) and the fact that MnO is difficult to be further reduced,$^{14,45}$ the lower-temperature peak is accordingly attributed to the reduction of MnO$_2$/Mn$_2$O$_3$ to Mn$_3$O$_4$, and the higher-temperature peak is ascribed to the further reduction of Mn$_3$O$_4$ to MnO and the reduction of surface ceria.$^{22}$ Moreover, it should be noted that there was only a slight increase of the reduction temperature over the pristine Ce–MnO$_2$, Ce–MnO$_2$(200), and Ce–MnO$_2$(300), that is, increase from 294 to 298 °C; however, the reduction temperature over Ce–MnO$_2$(400) significantly shifted to higher temperature (315 °C) as compared to the other three samples. Lower reduction temperature means a higher activity of oxygen vacancies, thus enhancing the reactivity of surface oxygen species. Therefore, it is reasonable to infer that the reactivity of oxygen vacancies decreased in the following sequence: Ce–MnO$_2$ ≈ Ce–MnO$_2$(200) ≈ Ce–MnO$_2$(300) > Ce–MnO$_2$(400).

3.2. Insights into the Effect of Heat Treatment on O$_3$ Decomposition. 3.2.1. Comparison of O$_3$ Decomposition at Room Temperature. The catalytic performance of the pristine and calcined Ce–MnO$_2$ is compared in Figure 8. Heat treatment at 200 °C had little effect on O$_3$ decomposition in comparison with the pristine sample, which demonstrates that the removal of tunnel water had little effect on O$_3$ removal efficiency. After 5-h reaction, their O$_3$ conversions dropped to ∼85%. According to the thermal analysis by Suib et al.,$^{19}$ most of the adsorbed water over todorokite MnO$_2$ exists in the tunnel, and on the basis of the thermal analysis (Figure 2) and XRD and Raman (Figure 3) results, 200 °C treatment can remove most of the tunnel water. However, in the activity evaluation system, the contact time of O$_3$ with the catalyst was very short (about 0.006 s as calculated from 1 L/min of feed gas and ∼0.1 mL of catalyst), which was not long enough for O$_3$ molecules to enter the tunnel. Thus, most of O$_3$ molecules were adsorbed and decomposed outside the tunnel, and the removal of tunnel water by 200 °C treatment has little effect on the O$_3$ decomposition performance. However, calcination at 300 °C greatly improved the catalyst stability. The Ce–MnO$_2$(300) sample kept ∼98% of removal efficiency for ∼115 ppm of O$_3$ during 5-h test under the space velocity of 1200 L g$^{-1}$ h$^{-1}$ at 25 °C. When the sample was heated at higher temperature (400 °C), the particle sintering (Figure 4G and H) and significant

Figure 6. Variations of Mn$^{3+}$/Mn$^{4+}$ and O$_{2u}$/(O$_{1}$+O$_{2u}$+O$_{3u}$) ratios with calcination temperature.

Figure 7. H$_2$-TPR profiles of the catalysts. Conditions: ∼50 mg of catalyst, 50 mL min$^{-1}$ of 5 vol % H$_2$/Ar, 5 °C min$^{-1}$.

Figure 8. Time dependences of O$_3$ conversion over the catalysts at room temperature. The used Ce–MnO$_2$(200) was regenerated at 200 °C for 3 h. Inset shows the long-term reaction over the pristine sample. Conditions: ∼50 mg of catalyst, feed gas of ∼1 L min$^{-1}$ of dry O$_3$ containing 110 ppm of O$_3$. 

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loss of oxygen vacancies (XPS in Figure 6 and H2-TPR in Figure 7) led to worse performance for O3 decomposition than the Ce−MnO2(300) sample.

In addition, according to the XRD patterns in Figure 3A, the particle size of CeO2 was estimated by the Scherrer equation. The particle sizes of CeO2 of the pristine Ce−MnO2, Ce−MnO2(200), Ce−MnO2(300), and Ce−MnO2(400) samples were calculated to be 2.5, 2.7, 2.6, and 3.3 nm, respectively. When the calcination temperature was ≤300 °C, the particle size of CeO2 was almost unchanged; however, the O3 surface adsorbed H2O did not increase with time when 20 mL of O3 was introduced into the IR cell, which demonstrates that the possible contribution of residual H2O in the pure O2 gas to the formation of surface adsorbed H2O during O3 decomposition could be excluded. Thus, the accumulation of surface adsorbed H2O during O3 decomposition very probably came from the reaction between Mn−OH and gaseous O3. As reported in the literature,46,47 O3 molecules did interact with the surface hydroxyl groups to form hydrogen bonds via one of the terminal oxygen atoms, although no reaction products (such as surface adsorbed H2O) were formed due to the fact that O3 adsorption was carried out at 77 K in these publications.

To further confirm the adverse effect of surface hydroxyl species on O3 decomposition, the used Ce−MnO2(200) sample was regenerated at 200 °C, and the regenerated sample was assumed to offer better catalytic performance than the fresh sample because O3 consumed the surface hydroxyl species and 200 °C treatment could remove the formed water. This assumption was confirmed as illustrated by curve 5 in Figure 8. What is more, according to the above assumption, the surface hydroxyl species will be completely consumed during O3 decomposition if the reaction time is long enough. Thereafter, the O3 removal efficiency will finally be stabilized. The long-term exposure to O3 gas was performed over the pristine Ce−MnO2. As shown in the inset in Figure 8, after 30-h reaction, the O3 conversion became almost constant around 80% due to the complete consumption of surface hydroxyl groups.

3.2.2. In Situ DRIFT Analysis. The changes of catalyst surface species during O3 decomposition were studied by in situ DRIFT. The time-resolved spectra over the pristine Ce−MnO2 are shown in Figure 9. As the reaction proceeded, the peak of Mn−OH species at 1273 cm−1 decreased with increasing intensity of the negative peak, indicating the gradual consumption of Mn−OH groups, while the peaks at 3408 and 1672 cm−1 ascribed to the surface adsorbed H2O gradually increased; that is, water accumulated on the catalyst surface. Besides, it can be seen from the inset that the intensity of surface adsorbed H2O did not increase with time when 20 mL min−1 of O2 was introduced into the IR cell, which emphasizes a versatile effect of surface hydroxyl groups and heat treatment on O3 decomposition. To further validate the deactivation mechanism of O3 decomposition catalysts involving surface hydroxyl groups, the pristine todorokite MnO2 without Ce modification was also treated at 300 °C for 3 h. The surface hydroxyl groups were greatly removed by 300 °C treatment, as indicated by the O 1s spectra in Figure S1. For MnO2 without Ce modification, 300 °C treatment can also greatly improve its stability for O3 decomposition (Figure S2). The in situ DRIFT study of O3 decomposition over the pristine MnO2 (Figure S3) also demonstrates that the surface hydroxyl groups were gradually consumed and the formed water was gradually accumulated over the catalyst surface during O3 decomposition. These are consistent with the results obtained with the Ce−MnO2 catalysts, indicating that the improvement mechanism of O3 decomposition performance by heat treatment at 300 °C is the same for MnO2 and Ce−MnO2 catalysts; that is, the lifetime...
improvement was mainly caused by the removal of hydroxyl groups from MnO₂.

3.2.4. Effect of \(O_3\) Concentration. When the inlet \(O_3\) concentration was lowered to about 7 ppm (Figure S4), the catalytic performance was greatly improved in comparison with Figure 8. However, the activity of the pristine Ce–MnO₂ still decreased with reaction time, and the 300 °C-treated sample showed stable \(O_3\) removal, which agrees well with the results in Figure 8. Therefore, it is tentatively deduced that the \(O_3\) decomposition mechanism and catalyst deactivation mechanism are independent from the \(O_3\) concentration. More experimental and theoretical research will be carried out systematically in future research.

On the basis of the above discussion, the effect of surface hydroxyl groups and heat treatment on \(O_3\) decomposition stability could be illustrated in Figure 10. Surface hydroxyl groups can react with \(O_3\), and the resultant water molecules occupy the active sites for \(O_3\) decomposition, leading to the decrease of catalytic activity. Because heat treatment at 300 °C could effectively remove surface hydroxyl groups without significant decrease of oxygen vacancies, the Ce–MnO₂(300) catalyst showed much better stability than the other three samples in this study. As Jia et al. previously suggested, oxygen vacancy is the active site for gaseous \(O_3\) decomposition, and the \(O_3\) decomposition performance largely depends on the amount of the oxygen vacancy. Also, surface hydroxyl group may be one kind of existing state of oxygen vacancy because oxygen vacancies may be occupied by oxygen, water, or its dissociative specie in the real environment. Thus, the present finding that surface hydroxyl group is not conducive to \(O_3\) decomposition indicates that the \(O_3\) decomposition depends not only on the amount of oxygen vacancies but also on their types and properties, which is helpful to develop more effective catalysts for \(O_3\) decomposition.

3.3. Gaseous \(O_3\) Removal over the Ce–MnO₂(300) under Dry and Low-Temperature Conditions. Commercial airliners typically cruise at altitudes where the environment is dry and low-temperature. So we investigated the performance of the Ce–MnO₂(300) sample under dry and low-temperature reaction condition. α-MnO₂ is generally considered as a kind of very active material for \(O_3\) removal; however, it can be seen from Figure 11A that the Ce–MnO₂(300) catalyst showed better \(O_3\) conversion than α-MnO₂ (XRD pattern of the as-obtained α-MnO₂ is shown in Figure S5) did for destructing dry \(O_3\) at 0 °C. Moreover, during long-term reaction over the Ce–MnO₂(300) sample (Figure 11B), the removal efficiency for 118 ppm of \(O_3\) was kept as high as 94% after 24-h reaction under a space velocity of 600 L g⁻¹ h⁻¹ at 0 °C, which demonstrates the potential application of the Ce–MnO₂(300) in real airliners.

4. CONCLUSIONS

The significant effect of heat treatment of Ce-modified tomodorokite-type MnO₂ (Ce–MnO₂) on gaseous \(O_3\) decomposition was found, and its mechanism was elucidated. In comparison with the pristine Ce–MnO₂, the sample treated at 200 or 400 °C did not show much better performance. However, the catalytic stability of the sample treated at 300 °C was greatly improved, and the removal efficiency for ~115 ppm of \(O_3\) was kept at ~98% at room temperature under a very high space velocity of 1200 L g⁻¹ h⁻¹ during the entire test. The in situ DRIFT study indicates that surface hydroxyl groups were consumed and water molecules were accumulated during \(O_3\) decomposition, accordingly decreasing the activity for \(O_3\) decomposition. Calcination at 200 °C could remove adsorbed water, but could not remove surface hydroxyl groups; calcination at 300 °C removed both water and hydroxyl groups, and at the same time the amount of oxygen vacancies (reaction sites for \(O_3\) decomposition) only slightly decreased; when the sample was heated at higher temperature (400 °C), the particle sintering and significant loss of oxygen vacancies led to worse performance for \(O_3\) decomposition. Finally, catalyst treated at 300 °C also exhibited highly stable \(O_3\) removal efficiency at temperature as low as 0 °C, which indicates its potential for practical application such as in a commercial airliner.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07931.

O 1s spectra of the pristine and 300 °C-treated MnO₃ comparison of \(O_3\) decomposition over the pristine and 300 °C-treated MnO₂, in situ DRIFT study of \(O_3\) decomposition over the pristine MnO₂, comparison of the pristine and 300 °C-treated Ce–MnO₂ for decomposition of ~7 ppm of \(O_3\), and XRD pattern of the as-obtained α-MnO₂ (PDF)
**Author Information**

**Corresponding Author**
*Tel.: +86 10 62773720. Fax: +86 10 62796840-602. E-mail: zpy@tsinghua.edu.cn.*

**ORCID**
Pengyi Zhang: 0000-0003-0344-0071

**Notes**
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**References**


