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Enhanced Catalytic Oxidation of Chlorobenzene over MnO₂ Grafted In Situ by Rare Earth Oxide: Surface Doping Induces Lattice Oxygen Activation

Lizhong Liu,* Ruoyu Liu, Tong Xu, Qiang Zhang, Yubin Tan, Qiaoling Zhang, Jiandong Ding, and Yanfeng Tang*



ABSTRACT: A series of highly active $MnO_2@REO_x$ (RE = Gd, Sm, Ce, and La) catalysts were successfully synthesized via in situ growth on the surface of MnO_2 , wherein the rare earth oxides were planted on the defect sites left by hydrogen peroxide etching of the surface of MnO_2 . Their physicochemical performance was investigated by scanning electron microscopy with energydispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), N₂ adsorption–desorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction with hydrogen (H₂-TPR), and temperature-programmed desorption of oxygen (O₂-TPD). The catalytic properties are compared through the catalytic oxidation of chlorobenzene. Among all catalysts, $MnO_2@$ GdO_x showed better mobility of surface lattice oxygen and higher molar ratios of Mn^{4+}/Mn^{3+} (1.10) and O_{ads}/O_{latt} (0.45), which promoted the superior low-temperature catalytic activity for chlorobenzene oxidation. The long-term chlorobenzene oxidation test (18 h) at different temperatures and the experiments with a mixture of VOCs showed that the as-prepared catalyst not only possessed a high stability but also was suitable for the efficient and simultaneous removal of multicomponent VOCs (toluene, benzene, acetone, and chlorobenzene). This work



also provided an idea for the further development of high-efficiency catalysts for the purification of VOCs from complex atmosphere environment.

1. INTRODUCTION

As a global air pollutant, volatile organic compounds (VOCs) are one of the main drivers of pollution such as urban haze, photochemical smog, and atmospheric toxicity.¹ Humangenerated emission of VOCs often originates from the tail gas of waste incineration, electric furnace steel-making, iron ore sintering, metal smelting, and coal-fired and coking industries, which generally contain a large number of chlorinated aromatic hydrocarbons, such as chlorobenzene with teratogenic, carcinogenic, and mutagenic hazards to the human body.²⁻⁴ Therefore, VOC emission is restricted by more and more strict regulations, which promotes paying more attention to the development of efficient control technologies.⁵ Catalytic oxidation technology has the advantages of low energy consumption, high purification, and less secondary pollution, so it is considered to be one of the most promising technologies for the industrialized treatment of VOCs.6-The focus of catalytic oxidation technology is catalysts.^{9,10} Although noble metals have high catalytic activity, their high cost, easy sintering at high temperature, and easy poisoning restrict their further application.^{11,12} Compared with noble metals, transition metal oxides have attracted much attention due to their low cost, good antitoxic properties, and wide sources.^{8,13,14}

As a kind of transition metal oxide, manganese dioxide has been widely studied due to its environmentally friendliness, low cost, and good catalytic activity for VOCs oxidation.^{15–17} It has been reported that the catalytic activity and stability of the heteroatom-modified manganese dioxide can better meet the requirements of different harsh conditions.¹⁸⁻²¹ Chen et al. synthesized manganese dioxide doped with iron and cerium, which were effective to remove the aromatic VOCs.^{22,23} He et al. prepared copper-doped manganese oxide catalysts and their results showed that the doping of copper into manganese oxides enriched the oxygen vacancies and increased the catalytic activity.²⁴ Cui et al. studied copper-doped manganese dioxide catalyst and found that the incorporation can tune oxygen vacancy concentration of MnO₂.²⁵ We also reported a modified manganese oxide catalyst with iron, and it exhibited excellent catalytic oxidation activity for toluene. However, it was also found that the catalytic activity for chlorobenzene was

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not enough.⁷ Less attention was paid to the fact that the catalytic oxidation of VOCs depends on the active species on the surface, and the active species located in the bulk cannot participate in the reaction. Besides, the difficulty of chlorobenzene oxidation is that chlorine ions easily invade the oxygen vacancies on the catalyst's surface, inhibiting the regeneration of adsorbed oxygen. Generally, the chloride ions can be extruded via lattice oxygen, but the required temperature is too high.²⁶ Hence, the question of how to modify the surface of MnO_2 with heteroatoms to enhance the low-temperature mobility of lattice oxygen is the key to improving the catalytic activity for the oxidation of chlorine-containing VOCs.

Rare earth elements have high oxygen affinity, which can provide catalysts with excellent oxygen transfer capabilities.²⁷ In this work, rare earth oxides $(GdO_{xy} SmO_{xy} CeO_{xy} and LaO_x)$ were directly grown in situ on the surface of manganese dioxide, wherein the hydrolysis of rare earth ions and the etching of manganese dioxide surface by hydrogen peroxide were carried out simultaneously. Combined with various characterization techniques (SEM-EDS, XPS, H₂-TPR O₂-TPD, etc.), the reason for the difference in the ability of different rare earth elements to activate lattice oxygen on the surface was revealed. Ultimately, the long-term evaluation of chlorobenzene oxidation as well as the catalytic oxidation of toluene, benzene, acetone, and mixed multicomponent VOCs over the preferred active catalyst were also explored.

2. EXPERIMENTAL SECTION

2.1. Preparation of Catalysts. A series of $MnO_2@REO_x$ (RE = La, Ce, Sm, and Gd) catalysts were synthesized by in situ growth of rare earth oxides on the surface of MnO_2 as shown in Scheme 1. A





typical preparation procedure of $MnO_2@GdO_x$ was as follows: First, 0.5 mmol (0.2234 g) of gadolinium nitrate hexahydrate was dissolved in 50 mL of 95% alcohol solution; afterward, 1.0 g of manganese dioxide was dispersed in the above solution by ultrasound. Then, 0.85 g (750 μ L) of a 30% hydrogen peroxide solution was added under continuous stirring. After 30 min, the mixed solution was filtered, and the obtained precipitate was heated to 450 °C for 3 h at a heating rate of 5 °C/min in a muffle furnace. The obtained sample was recorded as MnO₂@GdO_x.

For comparison, gadolinium nitrate hexahydrate was replaced with 0.5 mmol (0.2143 g) of lanthanum nitrate hexahydrate, 0.5 mmol (0.220 g) of samarium nitrate hexahydrate, and 0.5 mmol (0.2149 g) of ceric nitrate hexahydrate to obtain $MnO_2@LaO_{xy}$ $MnO_2@SmO_{xy}$ and $MnO_2@CeO_{xy}$ respectively. In addition, MnO_2 was prepared by a hydrothermal reaction according to previous researches (for details, see the Supporting Information, section S2).¹⁵

2.2. Catalytic Evaluation. The performance of catalysts for VOC oxidation was assessed in a successive-flow fixed-bed quartz microreactor (I.D. = 6.0 mm) with continuous heating. First, 0.2 g of sample powder was employed to test the activity. The stream with air, the saturated steam (RH = 100%), and 500 ppm of chlorobenzene were passed through the layer with a total flow rate of 100 mL/min. VOC conversion (α_{VOC}), CO₂ yield (Y_{CO_2}), and apparent activation energy (E_{ax} kJ/mol) were calculated by eqs 1–4:³²

$$r_{\rm VOC} = \frac{[C_x H_y]_{\rm in} \times \alpha_{\rm VOC}}{m_{\rm cat}}$$
(1)

$$r_{\rm CO_2} = \frac{[C_x H_y]_{\rm in} \times Y_{\rm CO_2}}{m_{\rm cat}}$$
(2)

$$E_{a}(VOC) = -R \times \frac{d(\ln r_{VOC})}{d(\frac{1}{T})}$$
(3)

$$E_{a}(CO_{2}) = -R \times \frac{d(\ln r_{CO_{2}})}{d(\frac{1}{T})}$$
(4)

where $[C_xH_y]_{in}$, r_{VOC} , r_{CO_2} , k_{VOC} , k_{CO_2} , $E_a(VOC)$, and $E_a(CO_2)$ are the concentration of VOC in inlet (mol/m³), reaction rates (mol/(g·s)) of VOC conversion and CO₂ yield, and apparent activation energies of VOC conversion and CO₂ yield.

3. RESULTS AND DISCUSSION

3.1. Characterization. All samples were characterized by SEM-EDS. It can be observed from SEM image in Figure S1 that the morphology of pure MnO_2 mainly presented as nanosheets, wherein some also contained a few nanorods. After the in situ modification via the rare earth elements, the morphology of each catalyst has not changed significantly (Figure 1a–d). Including Mn (Figure 1e–h) and O (Figure 1e–h)



Figure 1. SEM images of $MnO_2@GdO_x$ (a), $MnO_2@SmO_x$ (b), $MnO_2@CeO_x$ (c), and $MnO_2@LaO_x$ (d). EDS elemental mapping images of Mn from $MnO_2@GdO_x$ (e), $MnO_2@SmO_x$ (f), $MnO_2@$ CeO_x (g), and $MnO_2@LaO_x$ (h). EDS elemental mapping images of O from $MnO_2@GdO_x$ (i), $MnO_2@SmO_x$ (j), $MnO_2@CeO_x$ (k), and $MnO_2@LaO_x$ (l). EDS elemental mapping images of Gd from $MnO_2@GdO_x$ (m), Sm from $MnO_2@SmO_x$ (n), Ce from $MnO_2@$ CeO_x (o), and La from $MnO_2@LaO_x$ (p).

1i–l) elements, the EDS mapping images of $MnO_2@GdO_{xv}$ $MnO_2@SmO_{xv}$ $MnO_2@CeO_{xv}$ and $MnO_2@LaO_x$ showed the uniform distribution of Gd, Sm, Ce, and La elements (Figure 1m-p), suggesting that Gd, Sm, Ce, and La elements have been successfully inserted on the surface of MnO_2 . In addition, according to ICP analysis of samples, it can be confirmed that the rare earth elements have been successfully combined with MnO_2 (Table 1). In fact, rare earth ions (RE³⁺) are easily hydrolyzed in solution, thus forming the H⁺ ions and MnO₂@LaO.

MnO₂

0.79

0.64

4.71

4.73

531.25

531.32

Table 1. Surface Element Compositions and Hydrogen Uptake of MnO_2 , $MnO_2@CeO_x$, $MnO_2@LaO_x$, $MnO_2@GdO_x$, and $MnO_2@SmO_x$

 $RE(OH)_3$ precipitates (reaction I). The H⁺ ion generated by this can participate in the reaction between manganese dioxide and hydrogen peroxide (reaction II), causing the tetravalent manganese on the surface of the catalyst to be reduced into divalent manganese and leave the defect sites.⁵ Eventually, the combined reaction is completed, shown as reaction III. Besides, the resulting rare earth hydroxide colloids can be adsorbed into the defect sites by electrostatic action. After further treatment, the composites with rare earth were formed.

642.91

643.18

641.69

641.88

529.33

529.64

4.80

0

$$RE^{3+} + 3H_2O \leftrightarrow RE(OH)_3 + 3H^+$$
(I)

$$MnO_2 + 2H^+ + H_2O_2 \rightarrow Mn^{2+} + O_2\uparrow + 2H_2O \qquad (II)$$

$$3MnO_2 + 2RE^{3+} + 3H_2O_2$$

$$\rightarrow 3Mn^{2+} + 3O_2\uparrow + 2RE(OH)_3\downarrow \qquad (III)$$

Figure 2 displays the XRD patterns of MnO_2 , $MnO_2@GdO_x$, $MnO_2@SmO_x$, $MnO_2@CeO_x$, and $MnO_2@LaO_x$. The XRD



Figure 2. XRD patterns of MnO_2 , $MnO_2@GdO_x$, $MnO_2@SmO_x$, $MnO_2@CeO_x$, and $MnO_2@LaO_x$. Powder Diffraction File (PDF) no. 24-0735, Joint Committee on Powder Diffraction Standards (JCPDS).

patterns of all samples displayed the same diffraction characteristic peaks at $2\theta = 28.68$, 37.33, 41.01, 42.82, 56.65, 59.37, 67.24, and 68.55°, which corresponded to the (110), (101), (200), (111), (211), (220), (310), and (221) planes of MnO₂ (PDF no. 24–0735, JCPDS), indicating all catalysts showed the crystalline structures similar to that of MnO₂. Meanwhile, no other obvious diffraction peaks corresponding to GdO_{xy} SmO_{xy} CeO_{xy} and LaO_x were found.

 N_2 adsorption-desorption isotherms and pore-size distribution of all samples are shown in Figure 3a,b. The N_2

0.34

0.29

Article

48718

47241



Figure 3. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of MnO_2 , $MnO_2@CeO_x$, $MnO_2@LaO_x$, $MnO_2@GdO_x$, and $MnO_2@SmO_x$.

adsorption-desorption isotherms (Figure 3a) of MnO₂, MnO₂@CeO_{xt} MnO₂@LaO_{xt} MnO₂@GdO_{xt} and MnO₂@ SmO_x showed the typical IUPAC type IV pattern with a H3 type hysteresis loop, implying the existence of the slit nanopores formed by stacking layered nanoparticles.²⁸ Moreover, the pore size-distribution of all samples was between 2-10 nm (Figure 3b). Compared with MnO₂, the pore size distributions of MnO2@CeOx MnO2@LaOx MnO2@GdOx and $MnO_2@SmO_x$ were slightly shifted to larger pore sizes. As calculated by the BET method, the specific surface areas of each sample are 27.84 m^2/g for MnO₂, 19.13 m^2/g for $MnO_2@GdO_x, 20.82 m^2/g$ for $MnO_2@SmO_x, 21.44 m^2/g$ for $MnO_2@CeO_{xy}$ and 18.08 m²/g for $MnO_2@LaO_{xy}$ respectively. The slightly increase in pore size distribution and decrease in specific surface area may be due to the rare earth oxides (LaO_x, CeO_x , SmO_x , and GdO_x) loading on the surface of manganese dioxide.

In order to further explore the effect of different rare earth oxides on the surface characteristics of manganese dioxide, the oxidation states of Mn and active oxygen species on the surface of MnO2, MnO2@CeOx, MnO2@LaOx, MnO2@GdOx, and $MnO_2@SmO_x$ were obtained by XPS. The O 1s, Mn $2p_{3/2}$ and Mn 3s XPS spectra of all samples are displayed in Figure $4a-c_{1}$ and the quantitative analysis is shown in Table 1. As presented in Figure 4a, three components divided from Mn $2p_{3/2}$ XPS spectra of MnO_2 related to Mn^{4+} (643.18 eV), Mn^{3+} (641.88 eV), and Mn²⁺ (640.80 eV), respectively.^{7,29} After the rare earth elements were grown on the surface of MnO₂, the peak positions of Mn⁴⁺, Mn³⁺, and Mn²⁺ shifted toward a lower binding energy compared to that of MnO₂. It is suggested that the addition of rare earth oxides increased the electron cloud density of Mn⁴⁺, Mn³⁺, and Mn²⁺ on the surface of MnO₂.⁵ Meanwhile, we also found an increase of the Mn^{4+}/Mn^{3+} molar



Figure 4. (a) Mn 2p_{3/2}, (b) Mn 3s, and (c) O 1s XPS spectra of MnO₂, MnO₂@CeO_x, MnO₂@LaO_x, MnO₂@GdO_x, and MnO₂@SmO_x.

ratios in the order of 0.64 (MnO₂) < 0.79 (MnO₂@LaO_x) < 0.81 (MnO₂@CeO_x) < 0.98 (MnO₂@SmO_x) < (1.10) MnO₂@GdO_x. That is, MnO₂@GdO_x achieved the highest molar ratios of Mn⁴⁺/Mn³⁺ and had a better transformation of Mn⁴⁺ \leftrightarrow Mn³⁺, which is instrumental in the migration of active oxygen species and the catalytic oxidation of VOC.⁸ Rare earth elements have a strong oxygen affinity.^{27,29} During the formation of MnO₂@REO_x, this can cause the electrons in Mn–O to shift, thereby promoting the conversion of Mn³⁺ \rightarrow Mn⁴⁺. Meanwhile, the larger the electronegativity of rare earth oxide, the stronger the attraction of the rare earth element to oxygen; the increase of electronegativity follows the sequence of LaO_x < CeO_x < SmO_x < GdO_x.³⁰ Therefore, among the four rare earth modified catalysts, MnO₂@GdO_x should theoretically have the highest proportion of tetravalent manganese.

In addition, it can be observed from Figure 4b that the Mn 3s XPS spectra exhibits two separate peaks. The average oxidation state (AOS) of Mn on the surface of MnO_2 can be assessed by the magnitude of Mn 3s doublet splitting (ΔE_s) :^{16,31}

$$AOS = 8.956 - 1.126\Delta E_s$$
 (5)

As illustrated in Table 1, the AOS increases in the sequence of $MnO_2@GdO_x$ (4.336) > $MnO_2@SmO_x$ (4.316) > $MnO_2@CeO_x$ (4.266) > $MnO_2@LaO_x$ (4.246) > MnO_2 (4.226). The higher AOS also hints the higher fraction of Mn^{4+} , which is consistent with the characterization result of $Mn \ 2p_{3/2}$ XPS spectra.

The peaks from the O 1s XPS spectra of MnO₂ at 532.5, 531.32, and 529.24 eV belong to adsorbed oxygen species (O_{ads}) , lattice oxygen (O_{latt}) , and CO_3^{2-} or OH^- , respectively (Figure 4c).^{27,32} It can be found from Table 1 that the doping of rare earth oxides on the surface of MnO2 also caused a significant decrease in the binding energies of lattice oxygen and adsorbed oxygen, raising the electron cloud densities of O_{latt} and O_{ads}, which was conducive to the movement of lattice oxygen to the oxygen vacancy, thus removing the chlorine atoms from the oxygen vacancies. At the same time, it also helped the adsorbed oxygen species to attack the carbon cations (C^+) left via the dechlorination of chlorobenzene. Furthermore, the O_{ads}/O_{latt} molar ratios of five catalysts increased in the order of MnO_2 (0.29) < MnO_2 @LaO_x (0.34) $< MnO_2(a)CeO_x (0.36) < MnO_2(a)SmO_x (0.42) < MnO_2(a)$ GdO_r (0.45). In situ modification of Gd on the surface of manganese dioxide can increase the adsorbed oxygen content to a greater extent, suggesting that $MnO_2@GdO_x$ has a better catalytic activity for chlorobenzene oxidation. This may be related to the smallest radius of Gd³⁺ ion among the four rare earth ions. The differences between the radii of Gd^{3+} (0.094) nm) and those of Mn^{4+} (0.053 nm), Mn^{3+} (0.058 nm), and

 Mn^{2+} (0.067 nm) are smaller than those of La³⁺ (0.103 nm), Ce³⁺ (0.102 nm), and Sm³⁺ (0.096 nm) and Mn⁴⁺, Mn³⁺, and Mn²⁺. During the formation of the composites, the manganese ions removed by the hydrogen peroxide can enter the lattice gap of the rare earth oxides. The smaller radius gap between manganese and rare earth ions was more likely to cause the distortion of crystal structure of rare earth oxides, thereby increasing the surface oxygen vacancies and enhancing the surface adsorbed oxygen content. In addition, the analysis of the catalyst surface by XPS can also reveal the presence of Gd, Sm, Ce, and La elements (Figure S2).

 O_2 -TPD technology can directly reflect the type and mobility of oxygen species on the catalyst's surface. As revealed in Figure 5a, after the manganese dioxide was



Figure 5. O_2 -TPD profiles of MnO₂, MnO₂@GdO₃, MnO₂@SmO₃, MnO₂@CeO₃, and MnO₂@LaO₃: (a) 50-820 °C; (b) 50-500 °C.

modified with Gd, Sm, Ce, and La, its characteristic peak of oxygen in bulk at 536 °C shifted up to 30 °C for MnO2@ GdO_x, 29 °C for MnO₂@SmO_x, 26 °C for MnO₂@CeO_x, and 24 °C for MnO₂@LaO_x, respectively, which indicated that the formed rare earth oxides films on MnO₂ surface hindered the overflow of bulk oxygen. Considering that during the catalytic reaction the migration temperature of active oxygen was usually below 500 °C, the O2-TPD profiles of all catalysts below 500 °C were further analyzed (Figure 5b). These peaks of MnO₂ belong to physisorbed molecular oxygen (141 °C), chemisorbed oxygen atoms on the surface (199 °C), and oxygen in surface lattice (395 °C), respectively.^{5,7} After doping of Gd, Sm, Ce, and La ions, the peaks corresponding to the physisorbed molecular oxygen and oxygen in surface lattice moved toward a lower temperature, while the peak corresponding to the chemisorbed oxygen atoms transferred to a higher temperature. The loading of rare earth oxides on the surface of MnO₂ caused the reduction in the specific surface area, weakening the catalyst's capability of adsorbing O_{2} , dropping the desorption temperature of O_{2} on the catalyst surface. Besides, the increase in desorption temperature of the

catalysts with rare earth elements can be attributed to the strong attraction of rare earth oxides. More importantly, the doping of rare earth elements induced the desorption of surface lattice oxygen at a lower temperature, which facilitated the rapid migration of surface lattice oxygen into oxygen vacancies for the removal of chlorine atom from the oxygen vacancies, thereby restoring the relationship of conversion regeneration between oxygen vacancies and adsorption oxygen, further maintaining the high degradation of chlorobenzene.

Figure 6 shows the H₂-TPR profiles of MnO_2 , $MnO_2@$ GdO_x, $MnO_2@SmO_x$, $MnO_2@CeO_x$, and $MnO_2@LaO_x$. For



Figure 6. H₂-TPR profiles of MnO_2 , $MnO_2@GdO_{x'}$, $MnO_2@SmO_{x'}$, $MnO_2@GdCeO_{x'}$ and $MnO_2@LaO_{x'}$.

MnO₂, the characteristic peaks at 331 and 420 °C correspond to the reduction of Mn⁴⁺ → Mn³⁺ and Mn³⁺ → Mn²⁺, respectively.^{5,33} However, when MnO₂ was modified with GdO_x, SmO_x, CeO_x, or LaO_x, both of the above characteristic peaks appeared to move significantly toward a higher temperature, showing that the formation of rare earth oxides films on the MnO₂ surface delayed the reduction of manganese ions.³⁴ In addition, the H₂ consumption of Mn⁴⁺ → Mn³⁺ for the five catalysts is also calculated. As shown in Table 1, the order of the increase in H₂ consumption is as follows: MnO₂ (47241 mmol/g) < MnO₂@LaO_x (48718 mmol/g) < MnO₂@ CeO_x (49050 mmol/g) < MnO₂@SmO_x (49367 mmol/g) < MnO₂@GdO_x (50693 mmol/g). This result was consistent with that of XPS. It also suggested that rare earth oxides with strong electronegativity had a better ability to induce the formation of high valence manganese on the catalyst' surface.

3.2. Catalytic Activity Test. Before performance evaluation, the influence of interal and exteral diffusion and mass transfer have been excluded. Figure 7a emerges the activity comparison of chlorobenzene oxidation over different catalysts. As the catalytic reaction temperature continued to increase, the catalytic activity of all samples increased. Among them, the catalytic activities of SmO_{xy} GdO_{xy} and LaO_x were poor, and increasing the reaction temperature did not significantly improve their catalytic activity. Over the entire reaction temperature range, the catalytic activities of catalysts modified by rare earth elements for the conversion of chlorobenzene were higher than the activity of MnO₂ and the decreasing activity of modified catalysts in the catalytic oxidation of chlorobenzene was in the order of $MnO_2 @GdO_x > MnO_2 @$ $SmO_x > MnO_2@CeO_x > MnO_2@LaO_x$. Gd-modified manganese dioxide has a higher ability to catalyze the oxidation of chlorobenzene. The degradation of chlorobenzene first occurs with the cleavage of the C-Cl bond.³⁵ When chlorobenzene molecule is close to the catalyst's surface, the chlorine atom is easily captured by oxygen vacancies, thus remaining in the oxygen vacancies after the breaking of C-Cl bonds. If the



Figure 7. (a) Chlorobenzene conversion vs reaction temperature over different catalysts. (b) CO_2 yield from chlorobenzene oxidation vs reaction temperature over different catalysts. Dynamic study into the behavior of different catalysts in oxidization of chlorobenzene (c) and the yield of CO_2 (d).

chlorine atoms cannot be removed quickly, then the oxygen vacancies would lose their capability to generate adsorbed oxygen.^{34,36} The above characterizations via XPS O₂-TPD and H₂-TPR showed that Gd modification brought better surface lattice mobility and helped to squeeze chlorine atoms out from the oxygen vacancies, thereby restoring the ability of the oxygen vacancies to produce adsorbed oxygen, promoting the catalytic oxidation of chlorobenzene. In addition, it is worth noting that when the reaction temperature is lower than 240 °C, the conversion of chlorobenzene over CeO_x is higher than that over MnO₂, which was attribute to the better oxygen storage capacity of cerium oxide than manganese dioxide.³⁷

The mineralization of chlorobenzene over different catalysts is shown in Figure 7b. With the increase in the reaction temperature, the CO₂ yields of all samples increased simultaneously. The CO_2 yields of SmO_x LaO_x and GdO_x were almost zero, indicating that the active oxygen on the surface of SmO_{xy} La O_{xy} and Gd O_x was difficult to activate in large quantities. The descending order of CO₂ yields for all samples is as follows: $MnO_2@GdO_x > MnO_2@SmO_x >$ $MnO_2@CeO_x > MnO_2@LaO_x > CeO_x > LaO_x \approx SmO_x \approx$ GdO_x . This sequence reflected the migration and conversion capacity of active species. High transfer efficiency between lattice oxygen, oxygen vacancy, and adsorbed oxygen is conducive to generating more active oxygen to attack chlorobenzene molecules, achieving high-efficiency mineralization. Moreover, the $T_{20\%}$, $T_{50\%}$, and $T_{90\%}$ values (temperature vs chlorobenzene oxidation of 20%, 50%, and 90%) were also applied to evaluate their performance. As shown in Table 2, the temperature values of CO₂ yield for all samples are obviously greater than that of chlorobenzene conversion, implying the presence of byproducts (e.g., alcohols and phenol species) in the low-temperature catalytic oxidation of chlorobenzene.³

The apparent activation energy (E_a) is an inherent characteristic of a catalyst which has nothing to do with the specific surface area, concentration, and temperature.³⁸ As displayed in Figure 7c,d and Table 2, the $E_a(\text{VOC})$ and $E_a(\text{CO}_2)$ of chlorobenzene oxidation increased in the order of $\text{MnO}_2(\text{@GdO}_x \text{ (43.24 and 51.31 kJ/mol)} < \text{MnO}_2(\text{@SmO}_x \text{ (43.24 and 51.31 kJ/mol)})$

| Tabl | le 2 | . C | Comparison | of | Catal | ytic | Activities | over | Different | Catal | ysts |
|------|------|-----|------------|----|-------|------|------------|------|-----------|-------|------|
|------|------|-----|------------|----|-------|------|------------|------|-----------|-------|------|

| | | conversion | | | CO ₂ yield | | apparent activation energy | | |
|------------------|----------------------|-------------------------------|----------------------|----------------------|-------------------------------|----------------------|---------------------------------------|--------------------------|--|
| samples | $T_{20\%}/^{\circ}C$ | $T_{50\%}/^{\circ}\mathrm{C}$ | $T_{90\%}/^{\circ}C$ | $T_{20\%}/^{\circ}C$ | $T_{50\%}/^{\circ}\mathrm{C}$ | $T_{90\%}/^{\circ}C$ | $E_{\rm a}({\rm VOC})~({\rm kJ/mol})$ | $E_{a}(CO_{2})$ (kJ/mol) | |
| $MnO_2@GdO_x$ | 216 | 261 | 308 | 240 | 282 | 320 | 43.24 | 51.31 | |
| $MnO_2 @SmO_x$ | 237 | 276 | 319 | 259 | 296 | 345 | 58.12 | 71.58 | |
| $MnO_2@CeO_x$ | 250 | 290 | 344 | 266 | 309 | 350 | 70.11 | 80.34 | |
| $MnO_2@LaO_x$ | 259 | 303 | 350 | 275 | 318 | n/a | 75.33 | 82.25 | |
| MnO_2 | 267 | 310 | n/a | 287 | 327 | n/a | 93.02 | 114.67 | |
| CeO _x | 281 | 337 | n/a | 337 | n/a | n/a | 87.09 | 119.17 | |

(58.12 and 71.58 kJ/mol) < MnO₂@CeO_x (70.11 and 80.34 kJ/mol) < MnO₂@LaO_x (75.33 and 82.25 kJ/mol) < MnO₂ (93.02 and 114.67 kJ/mol). This suggested that MnO₂@GdO_x had the best mobility of lattice oxygen and the highest ratio of adsorbed oxygen, which facilitated the considerable degradation of chlorobenzene over MnO₂@GdO_x. Meanwhile, by comparing the values of $E_a(VOC)$ and $E_a(CO_2)$, it can be found that the $E_a(CO_2)$ value of each catalyst is significantly higher than its $E_a(VOC)$ value, which is a result of the degradation of chlorobenzene being a multistep process. The conversion of chlorobenzene only requires the first step of C-Cl bond cleavage, but the continued oxidation to carbon dioxide requires more oxidative decomposition processes, for example, chlorobenzene \rightarrow phenol \rightarrow hydroquinone \rightarrow ... \rightarrow small molecule organic matter $\rightarrow CO_{2}^{34}$ which is obviously bound to consume more energy. Furthermore, by testing the catalytic activity of catalysts with different gadolinium content in the catalytic oxidation of chlorobenzene, it can be found that the catalytic activity of the obtained catalyst was the best when the input amount of gadolinium was 0.5 mmol (Figure S3). In addition, the activity comparison of $MnO_2(@GdO_x)$ with other catalysts is shown in Table S1.

The long-term stability of the best active catalyst $(MnO_2@GdO_x)$ was also studied. As shown in Figure 8, the stability test



Figure 8. Long-term stability of $MnO_2@GdO_x$ for catalytic oxidation of chlorobenzene at 300 and 325 °C.

can be divided into three intervals. In the first interval of 6 h, the catalytic reaction temperature was maintained at 325 °C, and the catalytic activity of $MnO_2(@GdO_x \text{ was maintained at over 99% of chlorobenzene conversion and over 94% of CO₂ yield. As the reaction temperature dropped to 300 °C, the conversion and mineralization of chlorobenzene obtained by <math>MnO_2(@GdO_x \text{ dropped to 84\% and 66\%})$, respectively. At the same time, the gap between the conversion of chlorobenzene and the yield of CO₂ in this interval increased significantly, indicating that the reduction of the reaction temperature led to a substantial decrease in the active oxygen content, which is insufficient to fully mineralize the chlorobenzene. In addition, when the reaction temperature was raised to 325 °C, the

conversion of chlorobenzene was also restored, but the yield of CO_2 decreased slightly. This shows that the part of active sites on the surface of $MnO_2@GdO_x$ were occupied by chlorine atoms after the cooling reaction. Although the temperature was subsequently increased, the current temperature of 325 °C did not push all the chlorine atoms out of the oxygen vacancies, which requires a higher reaction temperature. Moreover, from SEM-EDS elemental mapping images of $MnO_2@GdO_x$ after chlorobenzene oxidation (Figure S4), the presence of chlorine element can be observed, suggesting that chlorine was not easily removed from the surface. Besides, the $MnO_2@GdO_x$ also displayed a good recyclability (Figure S5).

In addition, the catalytic oxidation of toluene, benzene, and acetone were also investigated. As exhibited in Figure 9a-c,



Figure 9. Catalytic oxidation of (a) 1000 ppm toluene, (b) 1000 ppm benzene, (c) 1000 ppm acetone, and (d) a mixture of VOCs: acetone (440 ppm), toluene (159 ppm), benzene (147 ppm), and chlorobenzene (58 ppm) over $MnO_2@GdO_{x^*}$

 $MnO_2@GdO_x$ also shows high catalytic activity for each singlecomponent VOC. The lowest temperatures of completely mineralized VOCs over $MnO_2@GdO_x$ are 225 °C for toluene oxidation, 250 °C for benzene oxidation, and 225 °C for acetone oxidation. The difference between VOC conversion and CO_2 yield at various temperatures was relatively small, implying that $MnO_2@GdO_x$ catalyst had a good ability of catalytic oxidation of VOC in deep. Besides, considering that real exhaust, such as the exhaust from spraying and pharmaceuticals, usually contains a mixture of acetone, toluene, benzene, and chlorobenzene, the catalytic activity of $MnO_2@GdO_x$ on the mixture VOCs has also been studied. As demonstrated in Figure 9d, the mixed components can be completely converted at 350 °C. When the reaction temper-

ature was higher than 225 °C, the order of VOC conversion was as follows: acetone > toluene > benzene > chlorobenzene; when the reaction temperature was lower than 200 °C, the order of VOC removal was acetone > chlorobenzene > toluene > benzene. This change in the sequence may be related to the catalytic reaction mechanism at different reaction temperatures. At low temperature, the degradation of VOCs mainly relied on the mutual conversion between adsorbed oxygen and oxygen vacancies on the catalyst surface. The dissociation energy of C-Cl bond (96 kcal/mol on the phenyl group) is lower than that of C-H bond (110 kcal/mol on the phenyl group).³⁴ Therefore, the C–Cl is easier to break than C–H. When the reaction was located in a high temperature zone, the lattice oxygen on the surface of the catalyst would be greatly excited, which has an additive effect on the organic carbon chain, thereby increasing the conversion of toluene and benzene.

4. CONCLUSION

MnO₂@GdO_x, MnO₂@SmO_x, MnO₂@CeO_x, and MnO₂@ LaO_r catalysts were successfully prepared by in situ etching growth on a manganese dioxide surface. Combined with characterization via XPS, H2-TPR, O2-TPD, and the chlorobenzene oxidation, the effect of the modification of different rare earth elements on the surface structure and catalytic activity of catalysts were revealed. The improvement in physicochemical performance can be due to the higher concentration of surface structure defects and electronegativity. Lattice oxygen migration ability and the molar ratios of O_{ads}/ O_{latt} and Mn⁴⁺/Mn³⁺ change from high to low in the order of $MnO_2@GdO_x > MnO_2@SmO_x > MnO_2@CeO_x > MnO_2@$ $LaO_x > MnO_2$, consistent with the order of their catalytic oxidation of chlorobenzene. The systemic dynamic research indicated that the $E_a(VOC)$ and $E_a(CO_2)$ values of chlorobenzene oxidation over MnO2@GdOr (43.24 and 51.31 kJ/mol) were lower than those of MnO₂@SmO₂ (58.12 and 71.58 kJ/mol), MnO₂@CeO_x (70.11 and 80.34 kJ/mol), MnO₂@LaO_x (75.33 and 82.25 kJ/mol), CeO_x (87.09 and 119.17 kJ/mol), and MnO₂ (93.02 and 114.67 kJ/mol). Long-term stability tests and catalytic oxidation experiments of a mixture of VOCs showed that MnO₂@GdO_x is an excellent catalyst for VOC removal.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02197.

Chemicals and materials, characterization, SEM image of MnO_2 , XPS spectra of La, Ce, Sm, and Gd on the surface of MnO_2 , chlorobenzene oxidation over $MnO_2(a)$ GdO_x catalysts prepared by using different concentrations of gadolinium nitrate, summary of previous study on the conversion of chlorobenzene over Mnbased oxides, and SEM-EDS elemental mapping images of $MnO_2(a)GdO_x$ after chlorobenzene oxidation (PDF)

AUTHOR INFORMATION

Corresponding Authors

Lizhong Liu – Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR *China;* orcid.org/0000-0002-6171-8513; Email: lzliu@ntu.edu.cn

Yanfeng Tang – Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China; Email: tangyf@ntu.edu.cn

Authors

- **Ruoyu Liu** Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China
- **Tong Xu** Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China
- Qiang Zhang Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China
- Yubin Tan Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China
- **Qiaoling Zhang** Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China
- Jiandong Ding Nantong Key Lab of Intelligent and New Energy Materials, School of Chemistry and Chemical Engineering, Nantong University, Jiangsu Province, Nantong 226019, PR China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c02197

Notes

The authors declare no competing financial interest.

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