

# Boosting the Dispersity of Metallic Ag Nanoparticles and Ozone Decomposition Performance of Ag-Mn Catalysts via Manganese Vacancy-Dependent Metal–Support Interactions

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environmental protection and human health, and Ag-Mn catalysts have shown promising O<sub>3</sub> decomposition. Catalysts with Ag supported on porous cube-like  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> (Ag/Mn-C) with high utilization of Ag were prepared by the impregnation method and showed excellent O<sub>3</sub> decomposition activity. Physicochemical characterizations demonstrated that metallic Ag nanoparticles (Ag<sub>n</sub><sup>0</sup>) were mainly anchored on manganese vacancies, forming Ag–O–Mn bonds between Ag<sub>n</sub><sup>0</sup> and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C. The abundant manganese vacancies of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C can lead to Ag<sub>n</sub><sup>0</sup> with a smaller particle size and more uniform dispersion, thereby resulting in markedly enhanced O<sub>3</sub> decomposition performance compared to



 $Ag_n^0$  with a large particle size and uneven distribution on rod-like  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> (Ag/Mn-R). Under a relative humidity of 65% and a space velocity of 1,110,000 h<sup>-1</sup>, the conversion of 40 ppm O<sub>3</sub> over the 2%Ag/Mn-C catalyst within 6 h (98%) at 30 °C was more than twice as high as that of the 2%Ag/Mn-R catalyst (42%). The study provides guidance for the design of highly efficient Ag-based catalysts and the understanding of the microstructure of supported catalysts.

KEYWORDS: manganese oxide, silver, manganese vacancy, metal-support interaction, ozone decomposition

# 1. INTRODUCTION

Ground-level ozone  $(O_3)$  pollution in large- and medium-sized cities has been particularly acute in summer.<sup>1</sup> Commercial airliners flying in the stratosphere face serious O<sub>3</sub> pollution problems.<sup>2</sup> Many industrial applications, such as sterilization, bleaching, deodorization, and wastewater treatment, emit large amounts of O<sub>3</sub> exhaust.<sup>3</sup> The extensive use of electrical equipment, including air purifiers, printers, and electronic disinfectors, causes indoor O<sub>3</sub> exceeding regulatory limits.<sup>4</sup> O<sub>3</sub> pollution in the atmospheric environment and confined spaces can be controlled effectively by the catalytic decomposition technology.<sup>2,5,6</sup> Manganese oxides (MnO<sub>x</sub>) have been widely studied as effective O<sub>3</sub> decomposition catalysts.<sup>6-12</sup> In addition, Ag as an excellent active component has frequently been added to MnO<sub>x</sub> because of its relatively cheap price and excellent water vapor resistance.<sup>13-15</sup> Although Ag-Mn catalysts have been synthesized with high O<sub>3</sub> decomposition activity in preliminary studies, the utilization rate of Ag is very low, which is not conducive to industrial application.<sup>15</sup> Also, the influence of the dispersion of Ag on O<sub>3</sub> decomposition activity is still unclear. In addition, which factor determines the chemical state of Ag, how to tune the chemical state of Ag, and the interaction between Ag and  $MnO_x$  in Ag-Mn catalysts are not clear. Therefore, Ag-Mn catalysts with excellent O<sub>3</sub> decomposition performance and a high Ag utilization rate

need to be developed, and the relationship between the dispersion of  $Ag_n^0$  and its activity needs to be revealed to further guide the design of efficient catalysts. In addition, the essential reasons determine the chemical state of Ag and the interaction mechanism between Ag and MnO<sub>x</sub> in the Ag-Mn catalysts need to be revealed.

The choice and regulation of the support, addition of additives, and development of new preparation methods all substantially influence the chemical state of  $Ag.^{16-21}$  In essence, the chemical state of a noble metal closely correlates with the metal–support interaction. The interaction takes place at the interface between the supported metal nanoparticles and the support in the form of charge redistribution and mass transport, so the surface structure of the support is very important to the interaction.<sup>22</sup> The morphology is an important manifestation of the surface structure of Ag by virtue of the regulation of the chemical state of Ag by virtue.

Received:	August 26, 2021
Revised:	October 27, 2021
Accepted:	October 29, 2021
Published:	November 9, 2021





of support morphology-controlling strategies is helpful for the in-depth study of the interaction mechanism between Ag species and MnO<sub>2</sub>. Up to now, the mechanism by which the MnO<sub>r</sub> morphology influences the chemical state of Ag and the catalytic activity of various oxidation reactions has rarely been studied. Li et al.<sup>23</sup> studied the effect of different morphologies (wire-like, rod-like, and tube-like) of  $MnO_2$  on the interaction between Ag and MnO<sub>2</sub> and found that Ag particles on wire-like MnO<sub>2</sub> were homogeneously dispersed and existed as hemispherical particles because of the strong interaction between Ag particles and wire-like MnO<sub>2</sub>; this was beneficial for toluene oxidation because of the enhancement of catalytic oxidation ability and the generation of more lattice oxygen. Lu et al.<sup>24</sup> found that Ag/MnO<sub>2</sub> nanorods with better catalytic oxidation ability and more surface-active oxygen exhibited better activity and stability for the oxidation of HCHO than Ag/MnO<sub>2</sub> nanoparticles. However, the level of structural characterization in the above studies was very limited and insufficient to analyze the interaction mechanism of Ag and MnO<sub>x</sub> and its effect on the dispersion of Ag in detail.

This interaction is affected by the content and type of anchoring sites (hydroxyl or surface defects) for noble metals on the support.<sup>25,26</sup> The relevant research studies mainly focus on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CeO<sub>2</sub>, or TiO<sub>2</sub> supports.<sup>27-35</sup> Wang et al.<sup>27</sup> revealed that the anchoring sites for Ag species on nanosized  $\gamma$ - $Al_2O_3$  were the ample terminal hydroxyls of the (100) surface. Dutov et al.<sup>28</sup> proved that the molar ratio between hydroxyls on SiO<sub>2</sub> and silver would affect the silver dispersion on Ag/  $SiO_2$  catalysts. Hu et al.<sup>29</sup> found that the amount of surface defects on different crystal planes of CeO<sub>2</sub> determined the interaction between Pd and CeO2, which further affected the structure and chemical state of Pd. Many researchers demonstrated that surface defects on TiO<sub>2</sub> supports were effective anchoring sites for single atoms and nanoparticles of Au.<sup>30-32</sup> However, the anchoring sites of Ag species on Mn<sub>2</sub>O<sub>3</sub> supports have not been determined, and the detailed interaction mechanism between Ag species and Mn<sub>2</sub>O<sub>3</sub> supports at anchoring sites needs to be revealed.

In this study, Ag-Mn catalysts with excellent  $O_3$  removal efficiency and a high Ag utilization rate were developed. Then, the influence of the  $Ag_n^0$  dispersion on the  $O_3$  decomposition performance over Ag-Mn catalysts was observed. The anchoring sites of  $Ag_n^0$  on  $Mn_2O_3$  supports were determined, and the relationship between the content of anchoring sites and the dispersion of  $Ag_n^0$  was determined. In addition, the detailed interaction mechanism between  $Ag_n^0$  and the  $Mn_2O_3$  supports at anchoring sites was revealed. This study not only provides guidance for the exploitation of efficient catalysts for  $O_3$  decomposition but also provides a deeper understanding of the interaction mechanism between Ag and  $MnO_{xv}$  which can guide the subsequent development of supported Ag-Mn catalysts.

## 2. EXPERIMENTAL SECTION

The porous cube-like  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> ( $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C) and rod-like  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> ( $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R) supports were synthesized by a hydrothermal method followed by high-temperature calcination. Then, the Ag/Mn-C and Ag/Mn-R catalysts were synthesized by impregnating AgNO<sub>3</sub> solution on the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports, respectively. The detailed preparation procedures are shown in the Supporting Information. The detailed characterization methods and computational details are shown in the Supporting Information. The evaluation methods for O<sub>3</sub> decomposition activity were consistent with our previous work,<sup>15</sup> and the detailed evaluation procedures are shown in the Supporting Information. The weight space velocity (WHSV) was maintained at 840 or 1680 L  $g^{-1}$  h<sup>-1</sup> by using 100 or 50 mg of catalyst.

#### 3. RESULTS AND DISCUSSION

**3.1. Crystal Structures and Morphologies of Supports.** As shown in Figure S3, the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports had the same crystal structure and no discernible differences in crystallinity.<sup>36</sup> The N<sub>2</sub> adsorption–desorption isotherms of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports are shown in Figure S3. The isotherms of the two supports were type IV isotherms with a hysteresis loop of type H3.<sup>37,38</sup> The pore size distribution plot showed the characteristics of a wide pore size range from mesopores to macropores. The average pore size of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R (3.3 nm) was distinctly smaller than that of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C (32.6 nm). The specific surface areas of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports were 18 and 14 m<sup>2</sup>/g, respectively, which are not significantly different.

As shown in Figure S4 and Figure 1A,  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C mostly showed a porous cube-like structure consisting of nanoparticles, while  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R exhibited a uniform rod-like structure (Figure S4 and Figure 1E). The electron diffraction



Figure 1. HRTEM images of (A–D)  $\alpha\text{-}Mn_2O_3\text{-}C$  and (E–H)  $\alpha\text{-}Mn_2O_3\text{-}R.$ 



Figure 2. (A) Raman spectra and (B) Mn K-edge EXAFS spectra of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R catalysts.

	Table	1.	Positron	Lifetime	Parameters	of	$\alpha$ -Mn <sub>2</sub> O	з-С,	$\alpha$ -Mn <sub>2</sub> O <sub>3</sub>	-R,	and	4%Ag	/Mn-	C
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sample	$ au_1$ (ps)	$I_1$ (%)	$ au_2$ (ps)	I <sub>2</sub> (%)	$\tau_3$ (ps)	I <sub>3</sub> (%)
$\alpha$ -Mn <sub>2</sub> O <sub>3</sub> -C	$204.8 \pm 1.7$	$52.2 \pm 0.8$	396.1 ± 3.8	$47.0 \pm 0.8$	$2080 \pm 170$	$0.8 \pm 0.1$
$\alpha$ -Mn <sub>2</sub> O <sub>3</sub> -R	$206.6 \pm 5.5$	$57.5 \pm 2.6$	$379.0 \pm 11.0$	$41.4 \pm 2.6$	$1510 \pm 120$	$1.1 \pm 0.2$
4%Ag/Mn-C	$190.2 \pm 5.5$	$55.4 \pm 2.6$	$349.6 \pm 9.0$	$43.7 \pm 2.6$	$1489 \pm 88$	$1.0 \pm 0.1$

pattern indicated that the single-crystalline structure of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C was damaged as shown by its disordered diffraction spots (Figure 1B). However,  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R had regular diffraction spots (Figure 1F), indicating its single-crystalline nature. The deterioration of the single-crystalline structure of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C is conducive to the formation of defects.<sup>39</sup> Figure 1C,D shows that there are many twisted, rough, and amorphous areas with obscure lattice fringes on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, indicating that more defects were formed on its surface. However,  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R exhibited clear and regular lattice fringes, and the fringe spacing was 0.381 nm, representing the (211) crystal planes of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> (Figure 1G,H). It has been found that defects on some oxides, such as MnO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub>, are important anchor sites of noble metal atoms,<sup>29-32,40</sup> so it was speculated that Ag nanoparticles on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C would be more evenly distributed.

The surface structure of the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports was investigated by Raman spectroscopy (Figure 2A). The peaks at 197, 312, 640, and 696 cm<sup>-1</sup> represented the typical vibrations of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>.<sup>41-43</sup> The peak intensities of  $\alpha$ - $Mn_2O_3$ -C were weaker than those of  $\alpha$ - $Mn_2O_3$ -R, corresponding to more defects on the surface of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C determined by HRTEM. Figure S5 shows the Mn 3s XPS spectra of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R. Compared with the perfect  $\alpha$ - $Mn_2O_3$  structure,  $\alpha$ - $Mn_2O_3$ -C and  $\alpha$ - $Mn_2O_3$ -R have the same number of oxygen vacancies. Figure 2B shows the Mn K-edge XAFS results of the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports. The coordination peak at 1.47 Å of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, corresponding to the Mn–O coordination shell, was stronger than that of  $\alpha$ - $Mn_2O_3$ -R, indicating that there are more Mn–O coordination bonds and fewer oxygen vacancies on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C. In addition, the coordination peak at 2.71 Å of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, corresponding to the Mn–Mn coordination shell, was weaker than that of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R, indicating that there are more manganese vacancies on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C. Curve-fitting results (Figure S6 and Table S1) for Mn K-edge EXAFS also indicated that the coordination numbers of Mn–Mn on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C are lower than those on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R. The  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support was p-type semiconducting metal oxide (Table S2). Metal cation vacancies readily occur in p-type semiconducting metal oxide. Then,

positron annihilation spectroscopy was used to confirm the manganese vacancy concentration of the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ - $Mn_2O_3$ -R supports.<sup>40,44</sup> The similar positron lifetime spectra of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R (Figure S7) indicated that these two supports had similar defect types. After analyzing the spectra, three lifetime components were found on these two supports. The lifetime of three components  $(\tau_1, \tau_2, \text{ and } \tau_3)$ increased in turn, corresponding to the bulk lifetime, the positron annihilation at manganese vacancies, and the lifetime of large voids (defect clusters), respectively.<sup>40,44,45</sup> The relative intensity of positron lifetime peaks represents the content of defects. The manganese vacancy content  $(I_2)$  in the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support (47.0%) was higher than that in  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R (41.4%) (Table 1), confirming the presence of more manganese vacancies on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C. After Ag was supported on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C<sub>1</sub> the manganese vacancy concentration (I<sub>2</sub>) decreased from 47.0% to 43.7% (Table 1 and Figure S8), directly demonstrating that Ag nanoparticles were anchored on manganese vacancies.<sup>40</sup> Yang et al.<sup>40</sup> proved that there was electrostatic repulsion between Ag and Mn atoms with positive charge on MnO<sub>x</sub> without manganese vacancies, while Ag atoms were easily adsorbed on the manganese vacancies of MnO<sub>x1</sub> and the existence of manganese vacancies eliminated the spatial isolation between Ag atoms and O atoms, facilitating charge transfer between Ag and MnOx. Therefore, the presence of more manganese vacancies on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C should be favorable for bonding between Ag nanoparticles and the support.

**3.2.** Chemical States and Dispersity of Ag on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>. As shown in Figure S9, the crystal structure of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R did not change after loading with Ag. After loading 4% Ag on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R, Ag species existed in the form of metallic Ag (Figure S9).<sup>46</sup> To further confirm the nature of Ag<sub>n</sub><sup>0</sup>, all catalysts were observed by HRTEM. For 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C catalysts, Ag species existed in the form of nanoparticles of 3.2 ± 1.9, 5.7 ± 2.6, and 7.5 ± 4.4 nm, respectively (Figure 3A–C). With the increase in Ag loading, Ag nanoparticles gradually grew in size. The Ag nanoparticles on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C all displayed lattice fringes of 0.236 nm (Figure S10), representing



Figure 3. HRTEM images of (A, D) 1%Ag/Mn-C, (B, E) 2%Ag/Mn-C, (C, F) 4%Ag/Mn-C, (G, J) 1%Ag/Mn-R, (H, K) 2%Ag/Mn-R, and (I, L) 4%Ag/Mn-R.

the (111) plane of  $Ag_n^{0.47}$  For 1%Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts, the diameters of Ag nanoparticles were 9.8 ± 3.7, 14.8 ± 5.2, and 17.9 ± 6.8 nm, respectively (Figure 3G–I). The fringe spacing of  $Ag_n^0$  on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R was also 0.236 nm, representing the (111) planes of  $Ag_n^0$  (Figure S10). In addition, Ag nanoparticles were always in contact with  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C at an acute angle (Figure 3D–F), while the contact mode between Ag nanoparticles and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R was an obtuse angle (Figure 3J–L), which indirectly proves that there is a stronger interaction between Ag nanoparticles and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C.

diameter (*d*) and the dispersion (*D*) (*d* (nm) = 1.31/D),<sup>51</sup> the dispersion of Ag on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R was obtained (Table S2). The results indicated that  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C promoted Ag dispersion, consistent with the ICP and XPS results (Table S3), which was attributed to the greater density of manganese vacancies on the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support. In short, the existence of more manganese vacancies led to the exposure of more active sites of metallic Ag on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C. According to a previous report, Ag<sub>n</sub><sup>0</sup> are excellent active sites for O<sub>3</sub> decomposition,<sup>15</sup> so the Ag/Mn-C catalysts should exhibit better activity than the Ag/Mn-R catalysts for O<sub>3</sub> decomposition.

3.3. The Interaction between Ag and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>. To further study the reasons for the differences in Ag dispersion on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R, the XPS spectra were collected to study the interaction between Ag nanoparticles and the support. The Ag  $3d_{5/2}$  binding energies were 368.15, 368.20, and 368.23 eV for the 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C catalysts, respectively, all of which were lower than that on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R (368.50 eV) (Figure 4A,B). The binding energy of Ag  $3d_{5/2}$  on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R fell in the same position as that of Ag foil (Figure 4C), which indicated that the large Ag nanoparticles on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R were in the metallic state. The Ag 3d<sub>5/2</sub> binding energy on Ag/Mn-C moved toward the direction of low energy, indicating that small Ag nanoparticles on this support have partial positive charges because of electron transfer between  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and Ag atoms, thus forming Ag-O-Mn bonds between Ag nanoparticles and the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support and enhancing the metal-support interaction.

The Ag K-edge XAFS data for 4%Ag/Mn-R and 4%Ag/Mn-C further corroborated the above conclusions. The K-edge energy and edge step of the 4%Ag/Mn-C catalyst moved toward those of AgNO<sub>3</sub> (Figure 5A), which also proved that small Ag nanoparticles on this support carried a partial positive charge. As shown in Figure 5B, 4%Ag/Mn-R and 4%Ag/Mn-C both showed one main peak at about 2.7 Å, associated with the Ag–Ag coordination shell. Compared with 4%Ag/Mn-R, the Ag–Ag coordination peak of 4%Ag/Mn-C was significantly weaker, which was because the Ag nanoparticles on it are smaller. In addition, a coordination peak of the Ag–O shell appeared at about 1.5 Å, indicating that Ag–O–Mn bonds formed on the 4%Ag/Mn-C catalyst. Then, quantitative fitting of the EXAFS spectra of Ag foil, 4%Ag/Mn-R, and 4%Ag/Mn-



Figure 4. Ag 3d XPS spectra of (A) 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C catalysts and (B) 1%Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts. (C) Ag 3d<sub>5/2</sub> binding energy positions in the XPS spectra of 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C catalysts, 1%Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts, Ag foil, and AgNO<sub>3</sub>.



Figure 5. Ag K-edge (A) XANES and (B) EXAFS spectra for Ag foil, AgNO<sub>3</sub>, Ag<sub>2</sub>O, 4%Ag/Mn-C, and 4%Ag/Mn-R catalysts, (C) corresponding fits of the EXAFS spectra, and (D) WT of the EXAFS spectra in the R space for Ag foil, 4%Ag/Mn-C, and 4%Ag/Mn-R catalysts.

C (Figure 5C and Table S4) was carried out to obtain accurate coordination information and investigate the interaction between Ag nanoparticles and the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> support. The Ag-Ag coordination numbers for Ag foil, 4%Ag/Mn-R, and 4%Ag/Mn-C were found to be 12, 7.9, and 5.0 with bond lengths of 2.87, 2.86, and 2.86 Å, respectively, and the Ag-O coordination number for 4%Ag/Mn-C was 0.8 with a bond length of 2.05 Å. The above results indicated that each Ag atom on 4%Ag/Mn-C coordinated with five Ag atoms from the Ag nanoparticles and almost one (0.8) oxygen atom from the α-Mn<sub>2</sub>O<sub>3</sub>-C support. However, each Ag atom on 4%Ag/Mn-R was coordinated to nearly eight (7.9) Ag atoms from Ag nanoparticles and had almost no coordination with oxygen atoms from the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R support. Next, the wavelet transform (WT) analysis of the Ag K-edge EXAFS spectra (Figure 5D) was carried out to further demonstrate the above conclusion. In the WT contour plot of 4%Ag/Mn-C, the intensity maximum of the Ag-O contribution appeared at around 4 Å<sup>-1</sup> and was markedly stronger than that of 4%Ag/ Mn-R, confirming the formation of more Ag-O-Mn bonds on the 4%Ag/Mn-C catalyst. The formation of more Ag-O-Mn bonds between Ag nanoparticles and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C proved the stronger interaction between them.

Raman spectra were collected to observe the changes in the catalyst structure after loading with Ag, which could also indirectly prove the strength of the interaction between Ag and the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> support. The peaks at 647 and 699 cm<sup>-1</sup> correspond to the asymmetric and symmetric stretching of bridged oxygen species (Mn-O-Mn), respectively.<sup>41-43</sup> With the increase in Ag loading, a new peak at 622 cm<sup>-1</sup> corresponding to Ag-O-Mn bonding appeared on the  $\alpha$ - $Mn_2O_3$ -C support (Figure 6A,B), which was because of the formation of Ag-O-Mn bonds on the Ag/Mn-C catalysts. Then, the asymmetric stretching vibrations of Mn–O–Mn and Ag-O-Mn were calculated to confirm the formation of Ag-O-Mn bonds, which is basically consistent with the experimentally measured frequencies (Table S5). Therefore, the new band observed at 622 cm<sup>-1</sup> did correspond to Ag–O– Mn bonds. However, Ag-O-Mn bonds did not appear on the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R support with the increase in the Ag loading (Figure 6C,D). The above results were consistent with the HRTEM, XPS, and XAFS results, which further clarified the stronger interaction between Ag and the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support. The stronger interaction was attributed to the formation of more Ag–O–Mn bonds on manganese vacancies of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, corresponding to the aforementioned characterization results.

The reducibility of the catalysts is shown in Figure S12. In the reduction path of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> catalysts, Mn<sub>2</sub>O<sub>3</sub> is first reduced to Mn<sub>3</sub>O<sub>4</sub> and then to MnO. The first reduction peak of the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C catalyst was located at 321 °C. After Ag was loaded on the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support, the Ag nanoparticles with



Figure 6. Raman spectra of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C catalysts (A) before peak fitting and (B) after peak fitting;  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R, 1%Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts (C) before peak fitting and (D) after peak fitting.

partial positive charges are reduced first (Figure S13),<sup>51</sup> and then the occurrence of hydrogen overflow causes the temperatures of the first reduction peak of 1%Ag/Mn-C, 2% Ag/Mn-C, and 4%Ag/Mn-C catalysts to decrease to 252, 202, and 201 °C, respectively. By comparison, the temperatures of the first reduction peak of the 1%Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts decreased from 364 °C to 260, 273, and 273 °C, respectively. Increasing the loading amount of Ag on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R did not cause the temperature of the reduction peaks of Ag/Mn-R catalysts to show a further decrease, which may be because hydrogen overflow reached saturation on the 1%Ag/Mn-R catalyst. The above phenomenon indirectly demonstrated the weak interaction between Ag and the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R support. Comparing the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R supports, the degrees of decline of the first reduction peak on the 4%Ag/Mn-C and 4%Ag/Mn-R catalysts were 120 and 90 °C, respectively, which further proved that Ag and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C had a stronger interaction.

**3.4. Ozone Decomposition Performance.** The activity of Ag/Mn-C and Ag/Mn-R catalysts for O<sub>3</sub> decomposition was evaluated under a relative humidity (RH) of 65% and a WHSV of 840 L  $g^{-1}$  h<sup>-1</sup> (Figure 7A). For the same Ag loading amount, the 6 h activity of Ag/Mn-C catalysts was always

superior to that of Ag/Mn-R catalysts (Figure 7A). The O<sub>3</sub> decomposition activity of 2%Ag/Mn-C could reach 98% after 6 h, while that of 2%Ag/Mn-R was only 42% (Figure S14), which was due to the greater density of active sites of metallic Ag on Ag/Mn-C. Then, the 4%Ag/Mn-C and 4%Ag/Mn-R catalysts were tested for 64 h under dry gas or a RH of 65% to investigate their long-term stability (Figure 7B). Under dry conditions, the 4%Ag/Mn-C and 4%Ag/Mn-R catalysts showed 98 and 89% O<sub>3</sub> conversion after 64 h, respectively. Under a RH of 65%, the O<sub>3</sub> conversion of the 4%Ag/Mn-C catalyst was stable at 53% after 64 h, but the O<sub>3</sub> conversion of the 4%Ag/Mn-R catalyst continued to decrease to 10%, indicating that the 4%Ag/Mn-C catalyst had better water resistance and more stable O<sub>3</sub> decomposition performance. The greater stability of O<sub>3</sub> decomposition activity on the 4% Ag/Mn-C catalyst (Figures S16 and S17) was attributed to the stronger interaction between Ag nanoparticles and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C. To evaluate the catalytic decomposition ability of the 4% Ag/Mn-C catalyst for O<sub>3</sub> in practical application, the removal ability of O<sub>3</sub> at low concentrations was tested. The 4%Ag/Mn-C catalyst still had 99% conversion for 600 ppb O<sub>3</sub> after 600 min (Figure S18). By adjusting test conditions, the turnover frequency (TOF) of the 4%Ag/Mn-C catalyst at 30 °C under a



Figure 7. (A) Six hours of ozone conversion on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R, 1%Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts under a WHSV of 840 L g<sup>-1</sup> h<sup>-1</sup> and a RH of 65%; conversion of O<sub>3</sub> for (B) 4%Ag/Mn-C and 4%Ag/Mn-R catalysts under a WHSV of 840 L g<sup>-1</sup> h<sup>-1</sup> and a RH of 65% or dry atmosphere, (C) 4%Ag/Mn-C and 4%Ag/Mn<sub>2</sub>O<sub>3</sub> catalysts under a WHSV of 1680 L g<sup>-1</sup> h<sup>-1</sup> and a RH of 65% or dry atmosphere, (C) 4%Ag/Mn-C and 4%Ag/Mn<sub>2</sub>O<sub>3</sub> catalysts under a WHSV of 840 L g<sup>-1</sup> h<sup>-1</sup> and a RH of 65%, and (D) 2%Ag/Mn-C and 6%Ag/ $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> catalysts under a WHSV of 840 L g<sup>-1</sup> h<sup>-1</sup> and a RH of 65%. Conditions: 40 ppm O<sub>3</sub>, T = 30 °C.

RH of 65% is calculated to be 0.0141 s<sup>-1</sup>, which is much larger than that of the 4%Ag/Mn-R catalyst (0.0018 s<sup>-1</sup>) under the same conditions. Moreover, the 4%Ag/Mn-C catalyst still showed 98% O3 conversion after 6 h under a RH of 90% (Figure S19), which further demonstrated its excellent water resistance. In addition, the activity of 4%Ag/Mn-C (79%) was nearly twice that of our previously reported 4%Ag/Mn<sub>2</sub>O<sub>3</sub>  $(Mn_2O_3$  with irregular spherical morphology, Figure S20) catalyst (42%) within 6 h under a higher WHSV of 1680 L  $g^{-1}$ h<sup>-1</sup> (Figure 7C),<sup>15</sup> and the activity of 4%Ag/Mn-C was far superior to most of the previously reported manganese-based catalysts (Table S6). To put this in perspective, satisfactory  $O_3$ decomposition performance can be achieved with a lower Ag loading (2%) on the Ag/Mn-C catalysts (Figure 7D), which was one-third of Ag loading of our previously reported Ag/ $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> catalyst. The above results indicated that the utilization rate of Ag was higher on the Ag/Mn-C catalyst, and the application cost of the catalyst was significantly reduced. By adjusting the morphology of the supports, the interaction between Ag and the support and the chemical state of Ag can be successfully tuned, giving Ag species on the catalyst in the state with the best catalytic performance. Therefore, the study has great guiding significance for further improvement of the performance of Ag-Mn catalysts in future studies.

**3.5. The Reaction Mechanism of Ozone Decomposition on Ag\_n^0.** To better understand the decomposition mechanism for O<sub>3</sub> on the 4%Ag/Mn-C catalyst and the reason for the decrease in activity with time, a catalyst that had been reacted with  $O_3$  for 64 h (Figure 7B) was characterized to investigate changes in the dispersion and valence of the Ag nanoparticles. According to the results of XRD (Figure S21), XPS (Figure S22), and HRTEM (Figure S17), it can be seen that the intermediate oxygen species that cannot desorb rapidly during  $O_3$  decomposition promote the oxidation and dispersion of metallic Ag nanoparticles.<sup>15</sup> Therefore, the activity of the 4%Ag/Mn-C catalyst for  $O_3$  decomposition declined slowly after it reacted with  $O_3$  for a long time.

According to the above characterization results and many previous studies, 52-54 a possible mechanism of O<sub>3</sub> decomposition on Ag nanoparticles is proposed. The overall process of O<sub>3</sub> decomposition over metallic Ag nanoparticles is shown in the following reaction equations (steps 1-3). First,  $O_3$ molecules adsorb on metallic Ag nanoparticles. Second, absorbed O<sub>3</sub> molecules decompose to O<sub>2</sub> molecules, and the remaining atomic oxygen species  $(O^{2-})$  are adsorbed on active sites. Then, atomic oxygen species react with gaseous O<sub>3</sub> molecules, forming an adsorbed peroxide species  $(O_2^{2-})$  and an O<sub>2</sub> molecule. Finally, most of the adsorbed peroxide species quickly decompose to oxygen molecules, and the metallic Ag nanoparticles participate in the next reaction cycle, giving the 4%Ag/Mn-C catalysts excellent catalytic activity. However, the metallic Ag nanoparticles are also slowly oxidized by adsorbed intermediate oxygen species to form some oxidized Ag species (steps 4-6),<sup>54,55</sup> which will lead to a gradual decline in the activity of the 4%Ag/Mn-C catalysts. When metallic Ag nanoparticles are oxidized to Ag<sub>2</sub>O<sub>2</sub> the reaction can proceed

cyclically (steps 4–6) and the activity of the 4%Ag/Mn-C catalysts can remain stable over a period of time (Figure 7B). However, the activity is only stable at 53%, far less than the original activity of the metallic Ag nanoparticles. To reuse the catalyst, the 4%Ag/Mn-C catalyst was treated for 1 h at 300 °C under a N<sub>2</sub> atmosphere, and the results showed that the activity could be completely restored to the original state (Figure S23), which indicated that the catalyst has good application prospects.

$$O_3 + Ag_n^0 \to O^{2-}Ag_n^{2+} + O_2$$
 (1)

$$O^{2-}Ag_n^{2+} + O_3 \to O_2^{2-}Ag_n^{2+} + O_2$$
 (2)

$$O_2^{2-}Ag_n^{2+} \to Ag_n^{0} + O_2$$
 (3)

$$O^{2-}Ag_n^{2+} \to Ag_2O + Ag_{n-2}^{0}$$
<sup>(4)</sup>

$$Ag_2O + O_3 \rightarrow 2AgO + O_2 \tag{5}$$

$$2AgO + O_3 \rightarrow Ag_2O + 2O_2 \tag{6}$$

3.6. Implications and Future Direction of the Research. In this study, Ag-Mn catalysts with high utilization of Ag and excellent O<sub>3</sub> decomposition performance were prepared by adjusting the morphology of the support. Ag<sub>n</sub><sup>0</sup> with a smaller particle size and more uniform dispersion on the Ag/Mn-C catalysts exhibited better O<sub>3</sub> removal efficiency than the large  $Ag_n^{0}$  on the Ag/Mn-R catalysts because of the exposure of more active sites. It was demonstrated that  $Ag_n^{0}$ are mainly anchored by manganese vacancies, forming Ag-O-Mn bonds between  $Ag_n^0$  and the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> support. More manganese vacancies existed on  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C<sub>1</sub> and more Ag-O–Mn bonds formed between Ag and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C, so smaller Ag<sup>0</sup> were anchored on this support. This study provides new insights into the understanding of the microstructure of supported catalysts, especially in the interaction between the metal and the support.

Under a high WHSV of 1680 L g<sup>-1</sup> h<sup>-1</sup>, the O<sub>3</sub> removal rate of the 4%Ag/Mn-C catalyst (79%) was nearly double that of a 4%Ag/ $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> (Mn<sub>2</sub>O<sub>3</sub> with irregular spherical morphology) catalyst (42%) in our previous works, indicating that this catalyst has greater potential for use in decomposition of O<sub>3</sub> under high humidity and high space velocity. To put this in perspective, satisfactory O<sub>3</sub> decomposition performance can be achieved with a lower Ag loading (2%) on the Ag/Mn-C catalysts, which was one-third of Ag loading of our previously reported Ag/ $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> catalyst. This study provides guidance for the design of more efficient Ag-based catalysts. Subsequent research should focus on the development of Ag-Mn catalysts with high Ag utilization and stable ozone decomposition activity.

#### ASSOCIATED CONTENT

#### **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c05765.

Detailed catalyst characterization methods; detailed activity evaluation procedures;  $Mn_2O_{10}$  cluster model (Figure S1) extracted from the crystalline structure of  $Mn_2O_3$ ;  $MnAgO_{10}$  cluster model (Figure S2) created by replacing a Mn atom with a Ag atom in the  $Mn_2O_{10}$  cluster model; XRD patterns and  $N_2$  adsorption/

desorption isotherms (Figure S3), SEM patterns (Figure S4), Mn 3s XPS spectra (Figure S5), and corresponding fits of the EXAFS spectrum in the R space (Figure S6) of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C and  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R catalysts; positron lifetime spectra (Figures S7 and S8) of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C,  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-R, and 4%Ag/Mn-C catalysts; XRD patterns (Figure S9), HRTEM images (Figure S10), Mn 2p XPS spectra (Figure S11), and H<sub>2</sub>-TPR profiles (Figures S12 and S13) of Ag/Mn-C and Ag/Mn-R catalysts; conversion of O3 (Figure S14) on Ag/Mn-C and Ag/Mn-R catalysts under a RH of 65% and a WHSV of 840 L  $g^{-1}$   $h^{-1}$ ; conversion of O3 (Figure S15) on the 4%Ag/Mn-C catalyst; Ag 3d XPS spectra (Figure S16) and HRTEM images and size distribution histograms (Figure S17) of fresh and used 4%Ag/Mn-C and 4%Ag/Mn-R catalysts; conversion of 600 ppb O<sub>3</sub> (Figure S18) on 4%Ag/Mn-C catalysts; conversion of O3 (Figure S19) on 4%Ag/Mn-C catalysts under an RH of 90% and a WHSV of 840 L  $g^{-1}$   $h^{-1}$ ; SEM images (Figure S20) of  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> with irregular spherical morphology; XRD patterns (Figure S21) and XPS spectra (Figure S22) of fresh and used 4% Ag/Mn-C catalysts;  $O_3$  conversion (Figure S23) of fresh, used, and regenerated 4%Ag/Mn-C catalysts; curvefitting results of Mn K-edge EXAFS (Table S1) in  $\alpha$ - $Mn_2O_3$ -C and  $\alpha$ -Mn\_2O\_3-R catalysts; voltage test results (Table S2) of hot and cold ends in the  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub>-C support; HRTEM, ICP, and XPS results (Table S3) of 1%Ag/Mn-C, 2%Ag/Mn-C, and 4%Ag/Mn-C and 1% Ag/Mn-R, 2%Ag/Mn-R, and 4%Ag/Mn-R catalysts; curve-fitting results of Ag K-edge EXAFS (Table S4) in Ag foil, 4%Ag/Mn-C, and 4%Ag/Mn-R catalysts; calculated and experimentally measured frequencies  $(cm^{-1})$  of Mn–O stretching vibrations (Table S5); summary of activity (Table S6) of various MnO<sub>x</sub> catalysts for O<sub>3</sub> decomposition (PDF)

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#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The authors appreciate the support of the National Natural Science Foundation of China (NSFC) (nos. 52022104 and 21876191), the Cultivating Project of Strategic Priority Research Program of Chinese Academy of Sciences (XDPB1902), the Young Talent Project of the Center for Excellence in Regional Atmospheric Environment, CAS (CERAE202006), and the Youth Innovation Promotion Association, CAS (2017064). We are grateful for the use of beamlines BL14W1, SSRF and 1W1B, BSRF for XAFS experiments.

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16152