

Article

Structured Mesh-Type Pt/Mn/ γ -Al₂O₃/Al Catalyst Enhanced the CO Oxidation at Room Temperature by In Situ Generation of Hydroxyl: Behavior and Mechanism

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Abstract: Nowadays, Pt-based catalysts are widely applied in carbon monoxide (CO) removal at room temperature. However, the effects of abundant hydroxyl groups (OH*) on the decomposition of intermediate products and catalyst durability have rarely been studied. In this work, a novel hydroxyl-rich structured mesh-type Pt/Mn/ γ -Al₂O₃/Al catalyst using a water vapor treatment (WVT) strategy to generate OH* in situ was developed. Firstly, density functional theory (DFT) calculations indicated that Mn-modification enhanced the adsorption capacity of CO and reduced the work function and the energy barrier of the catalytic reaction. Meanwhile, the water molecule dissociation ability of the Pt catalyst was improved. Secondly, the effects of WVT on the selected catalysts were investigated, and a possible reaction mechanism was proposed. XPS, FTIR, and TG results showed that WVT increased the content of OH*. Moreover, in situ FTIR further indicated that the increase of OH* content could alter the reaction path (from carbonate to formate pathway), thus enhancing the activity and durability of the catalyst. The selected catalyst exhibited excellent durability with 100% conversion within 200 h for 1000 ppm CO at room temperature.



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Keywords: CO removal; manganese modification; in situ generation; hydroxyl rich; formate

1. Introduction

Carbon monoxide (CO) is mainly derived from incomplete combustion processes, including water heaters, automobile exhaust, hydrogen fuel cells, and fire incidents [1,2]. This gas poses a serious threat to human health, as it can combine with hemoglobin to block oxygen transport and oxygen utilization. This interference may lead to serious consequences such as memory loss, myocardial infarction, hypoxia asphyxia, and even death [3]. In recent years, the catalytic oxidation method has become the most promising approach in CO removal due to its low energy consumption, minimal secondary pollution, and high efficiency [4]. It is mainly divided into non-noble metal catalysts and noble metal catalysts. Noble metal catalysts have been widely studied due to their high activity at low temperatures [5,6]. Platinum atoms (Pt⁰) could effectively adsorb CO molecules [7] and accelerate the adsorption and activation of O₂ [8]. Moreover, it has been reported that carbonate (CO₃^{2−}) and formate (HCOO[−]) are the main intermediate products in the CO oxidation reaction system [9]. Li et al. [10] investigated the catalytic oxidation of CO over Au–Pt bimetallic catalysts. DRIFT analysis identified HCOO[−] as the key reactive

intermediate during CO oxidation. DFT calculations further revealed low energy barriers for both formate formation (0.20 eV) and decomposition (0.68 eV), which indicates its rapid conversion to CO₂. In contrast, carbonate (CO₃^{2−}) was found to accumulate as a stable byproduct due to the higher decomposition energy, potentially poisoning active sites and hindering catalyst regeneration. Moreover, HCOO[−] exhibits a greater oxidation propensity than CO₃^{2−} owing to its lower decomposition temperature, rendering it more favorable for low-temperature reactions [11].

CO catalytic oxidation on Pt catalysts has been widely studied. On hydrophobic supports, carbonate species serve as the primary intermediates in the CO oxidation process (carbonate pathway). However, at room temperature, carbonates are difficult to desorb from the catalyst surface [12]. As the reaction progresses, the accumulation of carbonates on the catalyst surface leads to decreased activity and durability [13]. However, on hydroxyl-rich carriers, abundant OH* could alter the reaction pathway, transforming the intermediate products into formate (formate pathway). Since HCOO* can be readily decomposed into CO₂ and H₂O on the catalyst at room temperature, studying the role of OH* on the catalyst surface is crucial. To enhance catalyst activity, numerous studies have focused on the presence of OH* on the catalyst surface, especially because the hydroxyl content of the Pt-based catalysts was lower, and the OH* was continuously consumed during the reaction [14]. Luo et al. [7] investigated the effect of −OH on Pt–Fe–(OH)_x catalysts. This catalyst could easily oxidize CO to HCOO*, which could be further decomposed into CO₂. Zhao et al. [15] synthesized a single atom Pt⁰ supported on MgO nanosheets (Pt-SA/MgO). The catalyst facilitated the activation of molecular oxygen and the formation of reactive oxygen species. In the presence of H₂O, oxygen vacancies promoted the dissociation of molecular H₂O on the surface of Pt-SA/MgO, generating the primary active oxygen species OH*.

Zhang et al. [16] reported that abundant oxygen vacancies in the manganese oxide (MnO_x) help to stabilize the loading of Pt⁰ and increase the number of surface hydroxyl radicals, thereby improving the performance of the catalyst. MnO_x has been widely utilized in VOC's oxidation due to its low cost, diverse crystal structures, high specific surface area, and abundant oxygen vacancies. Li et al. [17] synthesized four MnO₂ polymorphs (α-, β-, γ-, and δ-MnO₂) catalysts via hydrothermal method. It was found that γ-MnO₂ catalyst exhibited the highest catalytic activity at 175 °C, achieving 82% CO conversion. Li et al. [18] highlighted that the specific surface area was a crucial factor influencing the catalytic performance of the MnO_x catalysts. The specific surface area directly determines the accessibility and number of active sites on the catalyst surface, thereby affecting the adsorption and activation of the reactants.

At present, numerous studies focus on Pt catalysts at room temperature or lower, with most demonstrating excellent activities. Boronin et al. [6] studied the Pt/CeO₂ catalyst, which achieved 100% conversion of 0.2 vol.% CO at 0 °C under a space velocity of 240,000 mL·g_{cat}^{−1}·h^{−1}. The Pt/MnO₂ catalyst reported in the literature [19] exhibited a T₉₀ of 120 °C at a gas hourly space velocity (GHSV) of 200,000 mL·g_{cat}^{−1}·h^{−1} with 1 vol.% CO. Moreover, under 0.12 vol.% CO at room temperature and GHSV = 40,000 mL·g_{cat}^{−1}·h^{−1}, Pt/MnO₂ achieved approximately 25% CO conversion and maintained this performance over 12 h. The PtCo/CoO_x/Al₂O₃ developed by Lin et al. [13] achieved complete conversion of 1 vol.% CO under dry gas conditions at GHSV = 30,000 mL·g_{cat}^{−1}·h^{−1} at 70 °C. Additionally, when 3% H₂O was introduced into the gas stream, the catalyst still achieved complete CO conversion at room temperature. Yan et al. [20] investigated Pt-based catalysts supported on different crystalline phases of manganese oxides (α-, β-, γ-, and δ-MnO₂). The results demonstrated that the Pt/α-MnO₂(K) achieved complete (100%) CO conversion at 65 °C under dry conditions and at room temperature in a humid environment. Although

some similar catalysts could achieve 100% conversion at room temperature, there was a lack of durability test data. Nevertheless, as a key indicator of the practical application of catalysts, the lack of durability seriously affects the comprehensive evaluation of catalyst performance and the assessment of their practical application prospects.

On the other hand, traditional particle or powder catalysts exhibit poor mechanical properties, high mass transfer resistance, and significant pressure drops [21]. Although traditional monolithic catalysts address these shortcomings, their loading methods lack strong atomic-level bonding, resulting in the detachment of active components during on-off cycling or rapid thermal shock conditions. To solve this problem, in our previous work, a novel mesh-type structured γ -Al₂O₃/Al carrier by anodic oxidation technology was proposed [22]. This carrier featured a sandwich structure consisting of an intermediate Al layer and in situ grown γ -Al₂O₃/Al layers on both sides. The carrier exhibited flexibility and self-constructed flow channels, enhancing mass and heat transfer [23]. Moreover, this porous structure facilitated active component modification, ensuring full contact with the reaction gas.

In this work, a novel hydroxyl-rich structured mesh-type Pt/Mn_x/γ-Al₂O₃/Al catalyst was developed for CO oxidation at room temperature. First, DFT investigations were conducted to analyze the charge properties, the activation energy for the CO catalytic reaction, and the H₂O dissociation capability of the Mn-modified Pt/γ-Al₂O₃/Al. Second, a series of Pt/Mn_x/γ-Al₂O₃/Al was prepared. A strategy of in situ generation of the OH* by water vapor treatment was proposed to investigate the OH* self-generation behaviors. The specific surface area and dispersion of Pt particles were analyzed by N₂ adsorption-desorption, X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). Furthermore, the in situ generation of OH* and the possible reaction mechanism on the catalyst surface were examined through the Fourier transform infrared spectroscopy (FTIR), thermogravimetric (TG), and in situ FTIR. Finally, a 200-h durability evaluation was carried out to assess the role of OH* on the catalyst in the reaction system.

2. Results and Discussions

2.1. DFT Investigation of Water Dissociation and CO Oxidation Behaviors on Mn-Modified Pt-Based Catalysts

To predict the role of Mn-modification in facilitating charge transfer in CO catalytic oxidation, DFT calculations were initially conducted. Figure 1a illustrates the simulation diagram of H₂O molecules adsorbed on Pt(111), Pt-MnO₂, and MnO₂ sites. Figure 1b exhibits the dissociation energy barriers of H₂O on Pt(111), Pt-MnO₂, and MnO₂, which are 1.01 eV, 0.73 eV, and 0.71 eV, respectively. These results clearly indicate that MnO₂ promoted the dissociation of H₂O to OH* on Pt(111). The adsorption site and the dissociation energy barrier of H₂O on Pt(111) aligned with previous reports [24]. According to the literature [25], MnO₂ with abundant oxygen vacancies can regulate the wettability of the material interface, facilitating the dissociation of surface H₂O into OH*. Based on these findings, this study proposed a strategy of using the water vapor treatment method to achieve in situ generation of OH* and subsequently create a hydroxyl-rich environment on the surface of Mn-modified Pt-based catalysts.

Furthermore, the DFT results revealed that the adsorption energy of CO on Pt-MnO₂ was lower than that on Pt(111), indicating enhanced CO capture capability for catalytic reactions. As illustrated in Figure 1c, work functions were calculated to investigate charge transfer on the catalyst surface. The work functions of the Pt(111) and Pt-MnO₂ surfaces were 5.76 and 5.63 eV, respectively. The lower work function of Pt-MnO₂ indicated that electrons were more likely to escape from this surface, rendering it more active than Pt(111). Figure 1c exhibits the adsorption energy of CO on Pt(111) and Pt-MnO₂, which are

−1.75 eV and −3.14 eV, respectively. Therefore, the Pt–MnO₂ surface was more favorable for CO adsorption, which was consistent with the results of the work function. As shown in Figure 1d, the activation energy of Pt and Pt–MnO₂ for the catalytic oxidation of CO with hydroxyl is 1.76 eV and 0.29 eV, respectively. It shows that the Mn-modified catalyst exhibited a lower energy barrier for the CO oxidation reaction. MnO₂ enhanced the charge transfer efficiency on the Pt(111) surface, thus facilitating the adsorption of reactants and dissociation of OH*.

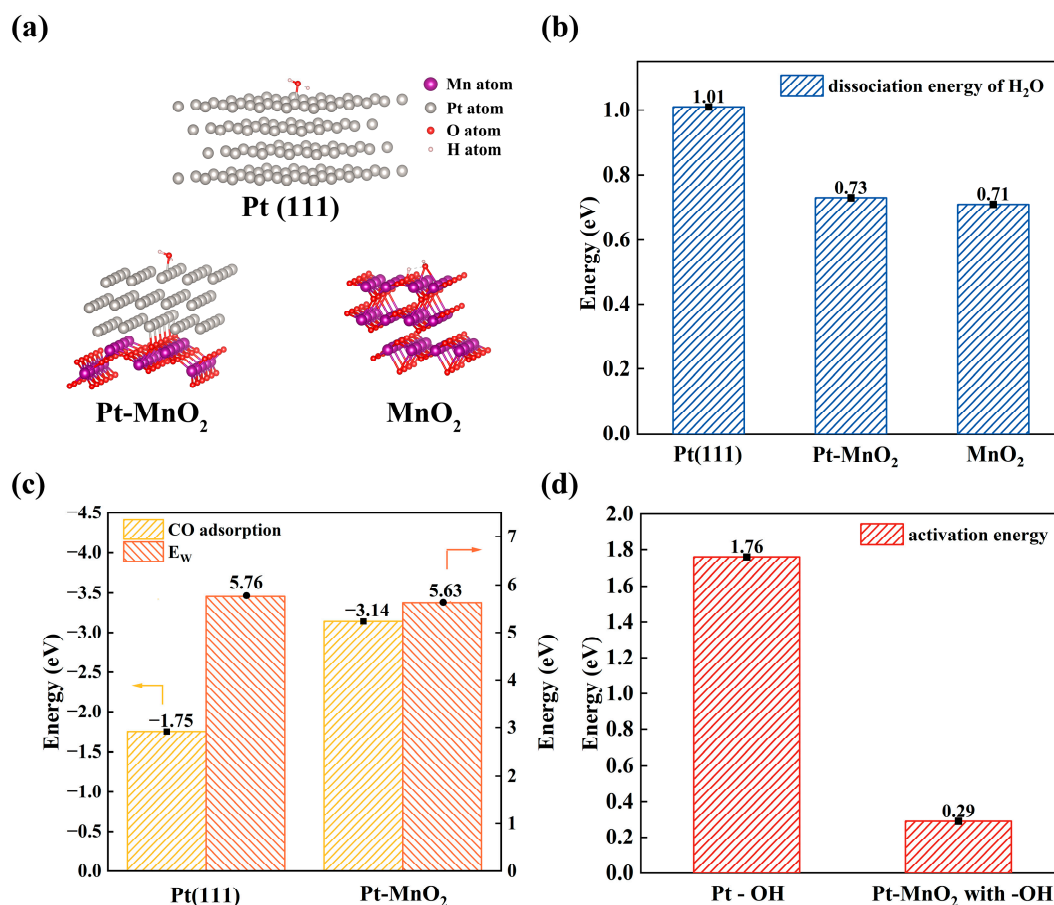


Figure 1. Simulation diagram of H₂O molecules adsorbed on Pt(111), Pt–MnO₂, and MnO₂ sites (a); dissociation energy of H₂O molecules on Pt(111), Pt–MnO₂, and MnO₂ sites (b); the adsorption energy of CO and work function (E_w) on Pt(111) and Pt–MnO₂ (c); activation energy for catalytic oxidation of CO on Pt–OH and Pt–MnO₂ with OH* interface (d).

2.2. Surface Properties of the Mesh-Type γ -Al₂O₃ Carrier and the Effect of Mn-Loading on Pt-Based Catalyst

Figure 2a–c presents the FESEM images illustrating the surface pore distribution of the mesh-type γ -Al₂O₃/Al carrier corresponding to the preparation sequence. As depicted in Figure 2a, an orderly hexagonal pore structure was formed on the aluminum substrate surface, which denotes ordered porous anodic alumina (AAO). The average diameter of the pores distributed on the carrier surface was 42 nm, and the specific surface area was 11 m²·g^{−1} [26]. As shown in Figure 2b, the AAO was hydrated for 1 h to obtain the anodic boehmite (AlOOH) support, which significantly increased the distribution of pores. The texture of the surface changed noticeably, revealing a three-dimensional honeycomb porous structure. As shown in Figure 2c, the final γ -Al₂O₃/Al carrier (Figure 2c) maintained similar structural features to AlOOH. As shown in Figure 2d (blue line), the γ -Al₂O₃ shows type IV isotherms with H2 hysteresis curves, indicating a characteristic mesoporous structure. The specific surface area of γ -Al₂O₃ increased from 11 m²·g^{−1} to 91 m²·g^{−1}.

due to the formation of a honeycomb porous structure. Moreover, it exhibited a narrow particle size distribution ranging from 3 to 15 nm (orange line in Figure 2d). Figure 2e displays the XRD pattern of γ - Al_2O_3 , confirming its successful preparation. Additionally, our previous study [27] demonstrated that γ - Al_2O_3 /Al possesses a higher density of Lewis acid sites. These Lewis acid sites are positively charged and can strongly adsorb metal anion precursors through electrostatic interactions, thereby inhibiting their migration and agglomeration [28]. The presence of Lewis acid sites (Al^{3+}) enhances the adsorption and dispersion of metal precursors (PtCl_6^{2-} ions).

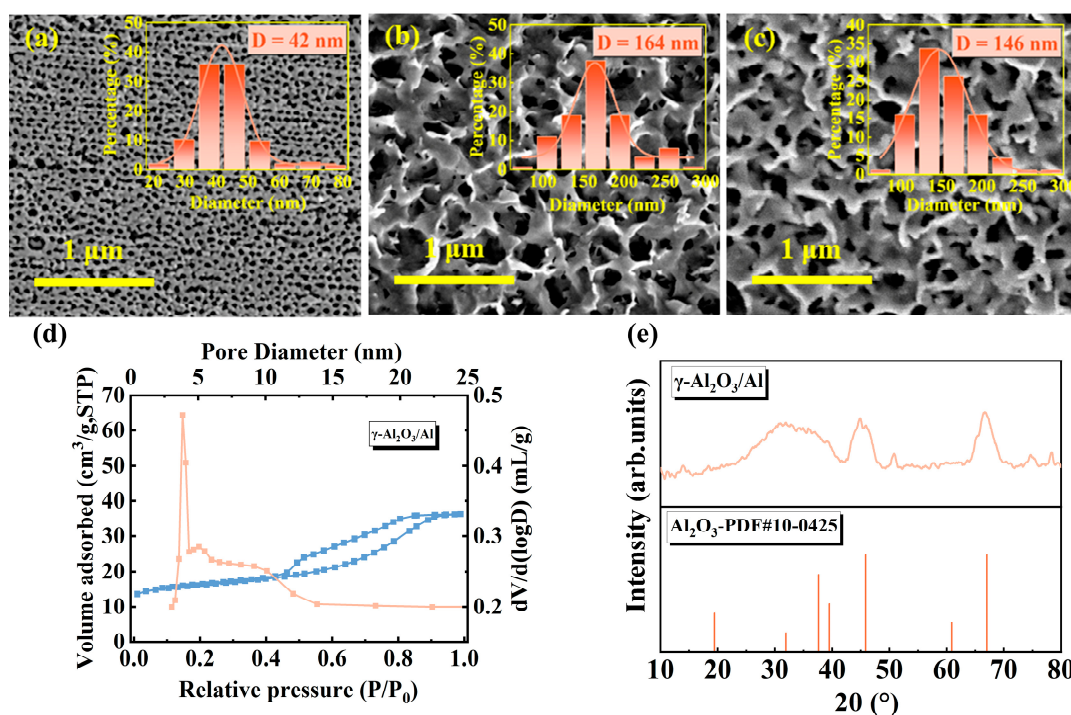


Figure 2. FESEM images of AAO (a), AlOOH (b), and γ - Al_2O_3 /Al carrier (c); N_2 adsorption/desorption isotherms (blue line) and pore-size distribution (orange line) of γ - Al_2O_3 /Al carrier (d); XRD patterns of γ - Al_2O_3 /Al carrier (e).

In this work, the novel mesh γ - Al_2O_3 /Al carrier was applied to develop the Mn-modified Pt-based catalysts. Different Mn-loading on Pt catalysts was adjusted by varying the concentration of the $\text{Mn}(\text{Ac})_2$. Figure 3 illustrates the catalytic performance of the prepared catalysts. First, the γ - Al_2O_3 /Al carrier was tested as a blank sample, which demonstrated minimal CO conversion of less than 10%. The Pt/ γ - Al_2O_3 /Al achieved an average CO conversion of 42% over 140 min but showed poor stability, declining to 20%. Compared with Pt/ γ - Al_2O_3 /Al, the Mn-modified catalysts displayed enhanced CO catalytic activity. With the increase of Mn loading, the activity increased initially and then decreased. The Pt/ $\text{Mn}_{4.7}$ / γ - Al_2O_3 /Al exhibited the best catalytic performance in this series, with an average CO conversion over 140 min that was 34% higher than that of Pt/ γ - Al_2O_3 /Al. This finding is consistent with the DFT results that the Mn-modified catalyst exhibited lower adsorption energy for CO. Furthermore, the Pt/ α - MnO_2 (K) catalyst reported in the literature [20] exhibited a 50% CO conversion (T_{50}) at 55 $^\circ\text{C}$ under dry conditions. In contrast, the catalyst developed in this study achieved a 76% conversion at room temperature. This enhanced performance demonstrated the research value of the Mn-modification in this study. Nevertheless, further improvements in both activity and durability were required to enable practical room-temperature applications. To optimize

performance and elucidate the key influencing factors, a water vapor treatment strategy was proposed. The effects of OH* on the reaction and the catalytic mechanism were analyzed.

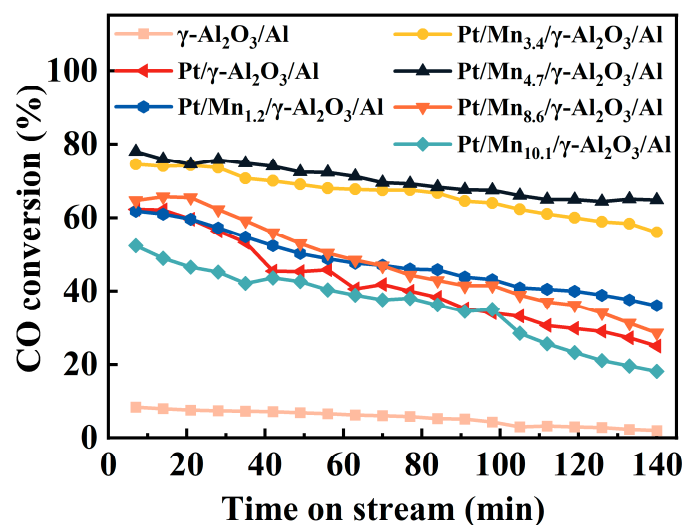


Figure 3. Activity performance of γ -Al₂O₃/Al, Pt/ γ -Al₂O₃/Al, and Pt/Mn_x/ γ -Al₂O₃/Al. (Condition: T = 25 ± 2 °C, m = 0.58 g, CO = 1000 ppm, WHSV = 26,000 mL·g_{cat}^{−1}·h^{−1}).

2.3. The Effects of Mn-Modification on Enhancing the CO Removal Efficiency by Water Vapor Treatment

N₂ adsorption-desorption was used to explore the microstructure and properties of the catalysts, as shown in Figure 4a. The pore size distributions of the catalysts ranged from 3 to 5 nm, with mesoporous structures predominating across all samples. The specific data are shown in Table 1. Compared with Pt/ γ -Al₂O₃/Al, Mn/ γ -Al₂O₃/Al showed larger pore volume and pore size. After the Mn-modified, the Pt/Mn/ γ -Al₂O₃/Al-WVT-0 exhibited the largest specific surface area of 164 m²·g^{−1}, which could provide more active sites and expose additional oxygen vacancies [29,30]. This increased surface area may contribute to the catalyst's lower water vapor dissociation energy. The Pt/Mn/ γ -Al₂O₃/Al-WVT-0 exhibited the smallest pore volume and pore size. After water vapor treatment, the catalyst showed a larger cumulative pore volume, and the surface material exhibited more pores, which was conducive to CO adsorption. The specific surface area of all catalysts showed a slight decrease, likely due to the formation of surface reconstruction.

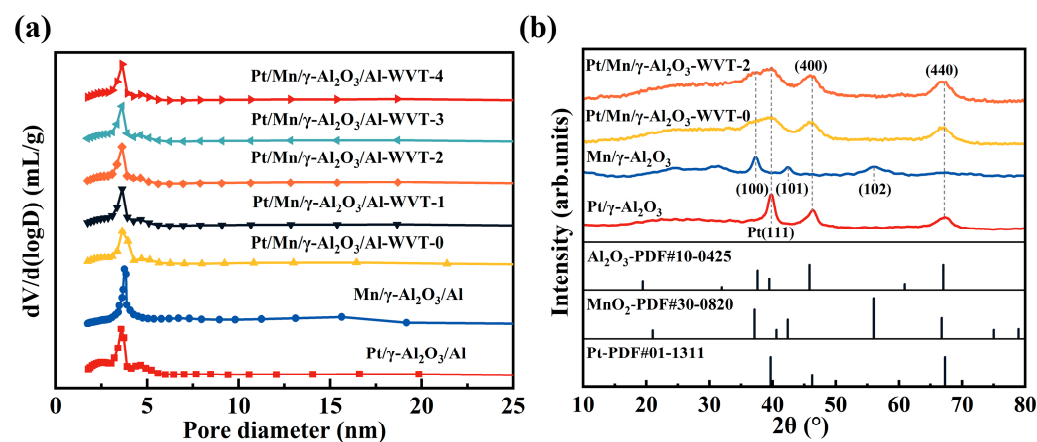


Figure 4. Pore diameter distribution curves (a) and XRD patterns (b) of different catalysts.

Table 1. Properties of different catalysts.

Catalysts	Pt Loading (wt.%)	Mn Loading (wt.%)	WVT ^a (h)	S _{BET} ^b (m ² ·g ^{−1})	V _{pore} ^c (mL·g ^{−1})	D _{pore} ^c (nm)
Pt/γ-Al ₂ O ₃ /Al	0.91	/	0	112	0.08	4.1
Mn/γ-Al ₂ O ₃ /Al	/	4.7	0	109	0.15	4.7
Pt/Mn/γ-Al ₂ O ₃ /Al-WVT-0	0.90	4.7	0	164	0.17	3.9
Pt/Mn/γ-Al ₂ O ₃ /Al-WVT-1	0.90	4.7	1	160	0.21	5.0
Pt/Mn/γ-Al ₂ O ₃ /Al-WVT-2	0.90	4.7	2	161	0.20	4.8
Pt/Mn/γ-Al ₂ O ₃ /Al-WVT-3	0.90	4.7	3	162	0.21	4.9
Pt/Mn/γ-Al ₂ O ₃ /Al-WVT-4	0.90	4.7	4	157	0.21	5.0

^a From the water vapor treatment time. ^b From the isotherm analysis in the relative pressure range of 0.04–0.12.

^c From the desorption curve of the BJH method.

Figure 4b displays the XRD patterns of the catalysts. Notably, two characteristic diffraction peaks were observed across all catalysts at 2θ angles of 45.9° and 67.0°. These peaks corresponded to the (400) and (440) crystal planes of γ-Al₂O₃ (JCPDS NO. 10-0425). All MnO₂-based catalysts showed broadened peaks, indicating poor crystallinity. The diffraction peaks at 37.1°, 42.4°, and 56.0° of Mn/γ-Al₂O₃/Al could be respectively indexed to the (100), (101), and (102) planes of ε-MnO₂ (JCPDS NO. 30-0820), respectively. The Pt/γ-Al₂O₃/Al displayed a diffraction peak of the Pt(111) crystal plane at 39.7°. In contrast, the diffraction peaks of the Pt/Mn/γ-Al₂O₃/Al-WVT-0 at the same position were relatively broad. This broadening of the peak shape can be attributed to the Mn-modification, which enhanced the dispersion of Pt particles on the surface of the carrier. In addition, the crystal structure of the catalyst remained unchanged after water vapor treatment; both Pt/Mn/γ-Al₂O₃/Al-WVT-0 and Pt/Mn/γ-Al₂O₃/Al-WVT-2 exhibited peaks of similar shape.

The FESEM images of Pt/Mn/γ-Al₂O₃/Al before and after water vapor treatment are presented in Figure 5. The catalyst without the water vapor treatment exhibited a polyhedral cubic structure measuring 5–8 μm in size, with a rough surface. The structure comprised a densely packed, non-overlapping monolayer of flat nanosheets that were stacked in a manner that created a uniformly distributed layered structure. This configuration provided the catalyst with a high specific surface area and abundant active sites, facilitating the adsorption of active components. As the duration of water vapor treatment increased, the originally uniform surface of the catalyst became more restructured. Some of the nanosheets were turned up to lay flat on the surface, and some agglomerations appeared. This observation is consistent with the slight decrease in the specific surface area of the catalysts, as indicated by the N₂ adsorption-desorption results shown in Table 1.

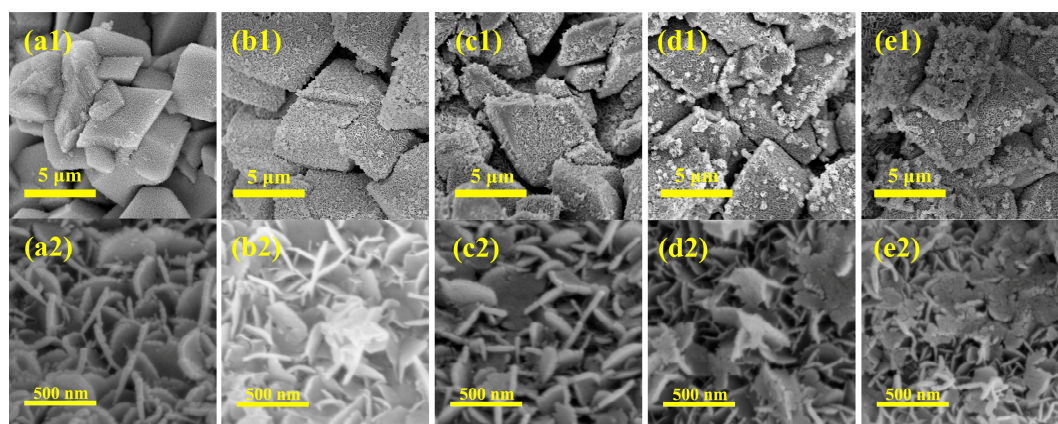


Figure 5. FESEM images of Pt/Mn/γ-Al₂O₃/Al-WVT-0 (a), Pt/Mn/γ-Al₂O₃/Al-WVT-1 (b), Pt/Mn/γ-Al₂O₃/Al-WVT-2 (c), Pt/Mn/γ-Al₂O₃/Al-WVT-3 (d), and Pt/Mn/γ-Al₂O₃/Al-WVT-4 (e).

To further observe the morphology of the catalysts and determine the size and dispersion of the particles, the surface structure of the catalyst was characterized by HRTEM. Figure 6 demonstrates the microstructure and morphology of the catalysts. The surfaces of the three catalysts displayed a nano-layered structure, with Pt nanoparticles uniformly distributed across the surface of the rod-like γ -Al₂O₃/Al support. This observation aligns with findings reported in the previous literature [31]. MnO_x could not be distinctly identified, probably due to its low degree of crystallinity. The Pt particles on the catalyst surface all exhibited a lattice spacing of 0.23 nm, which indicated the Pt(111) crystal plane. The results are consistent with the XRD results in Figure 4b.

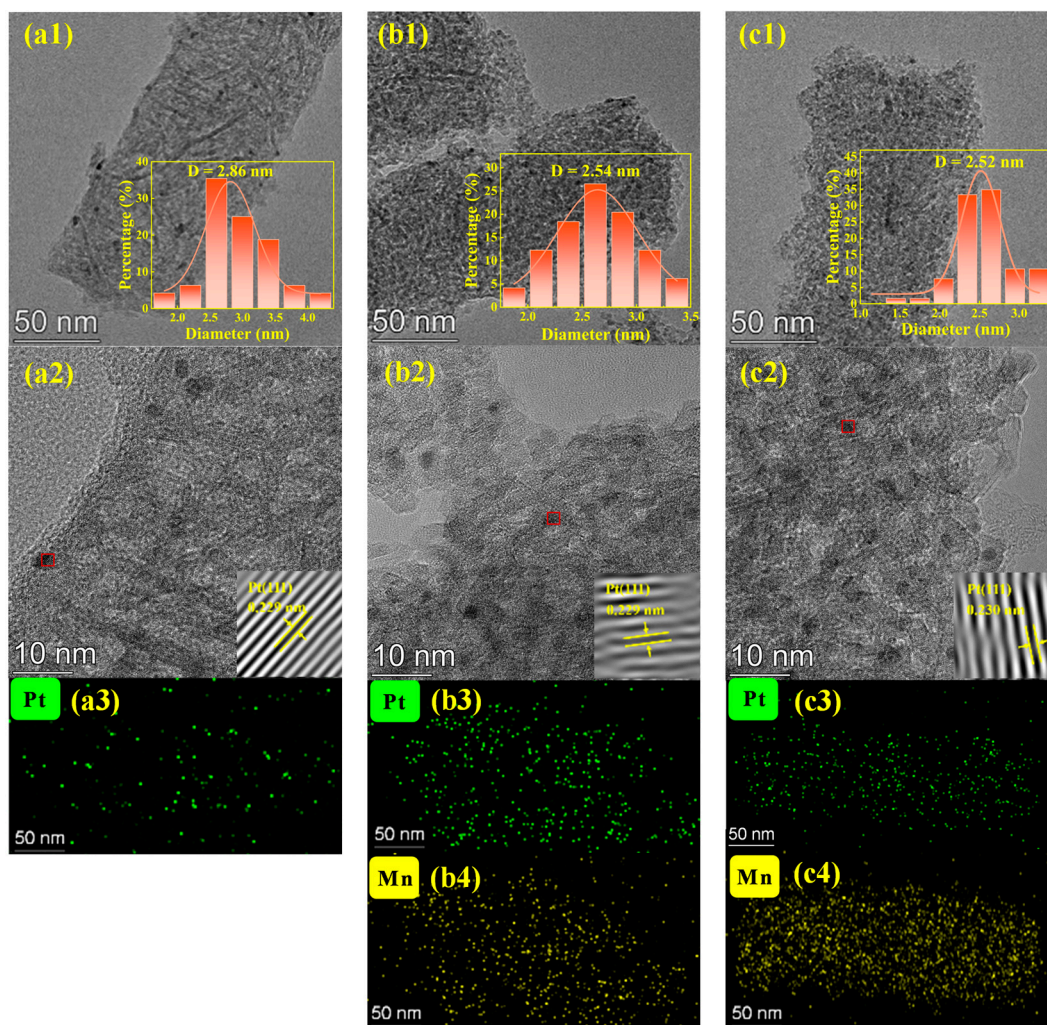


Figure 6. HRTEM images of Pt/γ-Al₂O₃/Al (a), Pt/Mn/γ-Al₂O₃/Al-WVT-0 (b), and Pt/Mn/γ-Al₂O₃/Al-WVT-2 (c).

The average sizes of Pt nanoparticles in Pt/γ-Al₂O₃/Al, Pt/Mn/γ-Al₂O₃/Al-WVT-0, and Pt/Mn/γ-Al₂O₃/Al-WVT-2 were 2.86 nm, 2.54 nm, and 2.52 nm, respectively. For comparison, the Pt particle sizes in Pt/γ-Al₂O₃/Al and Pt/Mn/γ-Al₂O₃/Al-WVT-0 were measured using the Scherrer formula as 3.21 nm and 2.76 nm, respectively. These results consistently demonstrated that Mn modification slightly reduced Pt particle size. XRD analysis confirmed this observation, showing that Mn modification broadened the Pt(111) diffraction peak, indicating improved dispersion of Pt particles. Noble metal catalysts with smaller particle sizes are preferred due to their enhanced catalytic activity for CO [32,33]. In smaller Pt nanoparticles, the electronic effect was more pronounced, which made more charge transfer and, thus, formed stronger chemical bonds. This observation is consistent

with the DFT calculations, which indicated that Pt-MnO₂ possesses a lower work function in comparison to Pt(111). Additionally, there was no significant change in particle size after water vapor treatment, indicating that water vapor did not affect the particle size of the Pt catalyst.

In addition, XPS was used to analyze the surface elemental valence and chemical composition of the catalysts. The high-resolution spectra of Mn 2p, Mn 3s, Pt 4f, and O 1s are shown in Figure 7. The quantitative analyses are summarized in Table 2. According to Mn 3s calculations, the AOS values ranged from 3.1 to 3.3, indicating that the catalysts were predominantly composed of Mn³⁺ and Mn⁴⁺. Mn 2p was fitted to three peaks at 640.8 eV, 642.2 eV, and 643.1 eV, which were attributed to the Mn²⁺, Mn³⁺, and Mn⁴⁺ species, respectively. The catalysts were mainly present in the valence state of Mn⁴⁺ in the form of MnO₂. This finding is consistent with the morphology of MnO₂ observed in the diffraction peaks in XRD. The existence of Mn²⁺ was due to the insufficient calcination of MnCO₃ at 400 °C.

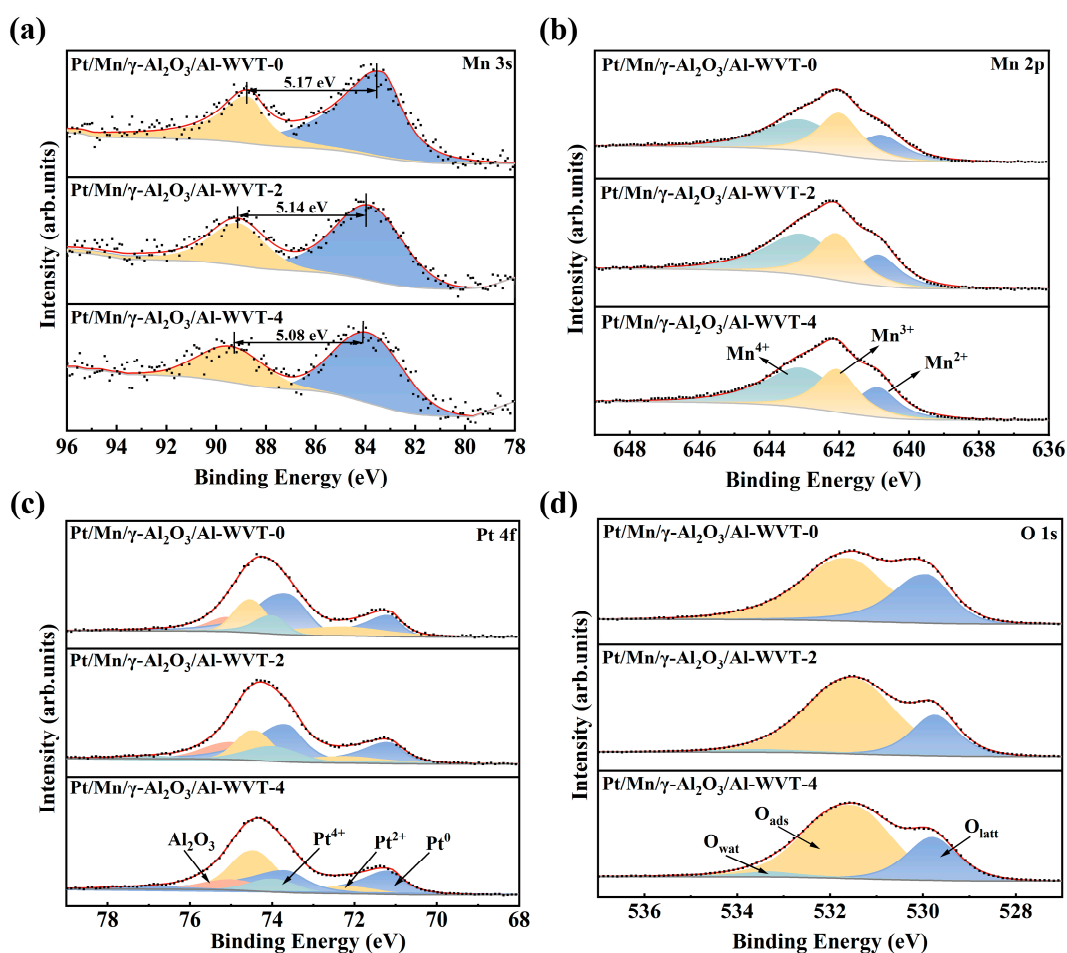


Figure 7. XPS results of Pt/Mn/ γ -Al₂O₃/Al-WVT-X (X = 0, 2, and 4) catalysts Mn 3s (a), Mn 2p (b), Pt 4f (c), and O 1s (d).

Table 2. XPS fitting of the Mn 3s, Mn 2p, Pt 4f, and O 1s peaks.

Catalyst	Mn 3s	Mn 2p		Pt 4f	O 1s
	AOS	Mn ³⁺ / Mn _{total}	Mn ⁴⁺ / Mn _{total}	(Pt ⁰ + Pt ²⁺ + Pt ⁴⁺)	(O _{latt} + O _{ads} + O _{wat})
Pt/Mn/ γ -Al ₂ O ₃ /Al-WVT-0	3.13	0.34	0.42	0.55	0.65
Pt/Mn/ γ -Al ₂ O ₃ /Al-WVT-2	3.17	0.31	0.45	0.50	0.74
Pt/Mn/ γ -Al ₂ O ₃ /Al-WVT-4	3.23	0.29	0.48	0.47	0.69

After the water vapor treatment, the AOS of the catalysts increased slightly, indicating that water purging could enhance the valence state of the catalyst. The content of Mn^{3+} gradually decreased, while that of Mn^{4+} increased. This indicated that the charge transfers of water molecules occurred on the catalyst surface. The Mn^{3+} cation was in agreement with the high-spin $3d^4$ electronic configuration, which could provide more than one free electron [34]. Mn^{3+} sites served as effective adsorption sites for oxygen species. According to the literature [29], the presence of Mn^{3+} in the catalyst leads to the generation of oxygen vacancies to maintain electrostatic balance. The specific equations are as follows:

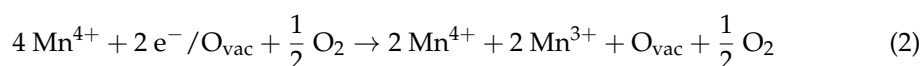
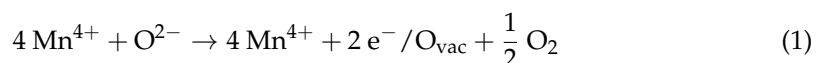


Figure 7c shows the Pt 4f spectra of the catalysts, with specific data detailed in Table 2. The Pt on the catalyst surface was mainly divided into three valence states: Pt^0 , Pt^{2+} , and Pt^{4+} . The peaks at 71.4 eV and 74.7 eV were attributed to Pt^0 species, the peaks at 72.9 eV and 76.2 eV were attributed to Pt^{2+} species, and the peaks at 74.3 eV and 77.6 eV were attributed to Pt^{4+} species. Because of the large amount of Al element in the carrier, the Al 2p peak was fitted around 75 eV [35]. With the increase in water vapor treatment time, the content of Pt^0 on the catalyst surface decreased slightly. The presence of water vapor slightly changed the adsorption properties on the catalyst surface, potentially leading to increased adsorption of oxygen or other substances, which resulted in a higher valence state [36].

The O 1s spectra of the catalysts are shown in Figure 7d. The asymmetric O 1s spectra could be fitted to three peaks. The peaks corresponding to lattice oxygen (O_{latt}), hydroxyl group (O_{ads}), and water molecules (O_{wat}) are 529.9 eV, 531.7 eV, and 533.5 eV, respectively. As shown in Table 2, with the prolonged water vapor treatment time, the hydroxyl peak showed a trend of increasing first and then decreasing. Pt/Mn/ γ - Al_2O_3 /Al-WVT-2 exhibited the highest OH* content of 74%.

FTIR was employed to analyze the distribution of functional groups on the catalyst surface following different durations of water vapor treatment, as illustrated in Figure 8a. All catalysts exhibited broad and intense absorption spectra in the range of 3100 cm^{-1} to 3700 cm^{-1} , which was attributed to the stretching vibrations of OH* on the catalyst surface. As the treatment time increased, the intensity of absorption peak in this range increased first and then decreased. This trend indicated that water vapor treatment increased the OH* content on the catalyst, with the highest OH* content observed at the Pt/Mn/ γ - Al_2O_3 /Al-WVT-2. FTIR characterization confirmed that water vapor treatment successfully in situ generated the OH* on the catalysts. These OH* groups played a crucial role in CO catalytic oxidation, OH* could react with adsorption CO (CO^*) to form formate species ($\text{OH}^* + \text{CO}^* \rightarrow \text{HCOO}^*$) [37]. Additionally, all catalysts exhibited intense absorption peaks at the 1650 cm^{-1} and 1410 cm^{-1} , corresponding to the H_2O and carbonates, respectively [38]. The presence of water indicated that the catalyst readily adsorbed H_2O . The carbonates observed were attributed to insufficiently calcined MnCO_3 on the surface of the catalyst, which aligned with the results of Mn 2p in XPS.

As shown in Figure 8b, TG tests were conducted to analyze the content of physically adsorbed water and OH* on the catalyst surface. Within the temperature range of 20 – 600°C , three weight-loss stages were observed. The first weight-loss stage (30 – 150°C) was attributed to the desorption of physically adsorbed water. The weight loss of the samples due to H_2O was nearly uniform, indicating that a portion of the H_2O adsorbed on the catalyst surface had been converted into OH*. The second stage (150 – 400°C) corresponded

to weight loss due to the breakdown of metal–OH structural hydroxyls [39]. This was reflected in the rise and subsequent decline of the hydroxyl peak area in the FTIR results. Regarding the decrease in OH* content, reference [40] indicated that although adsorbed H₂O could break the O–H bond to form abundant OH*, an excess of water molecules would recombine with OH*. This led to a decrease in the active sites and deactivation of the catalyst. The surface exhibited the highest hydroxyl amount on Pt/Mn/ γ -Al₂O₃/Al-WVT-2. The increased amount of OH* was advantageous for enhancing catalytic activity. The third stage (400–600 °C) involved weight loss primarily due to the cleavage of partial AlOOH and Pt–OH bonds on the catalyst surface at elevated temperatures [31], as well as the presence of inadequately calcined MnCO₃ and the crystal transformation of MnO_x [41]. TG and FTIR results indicated that water vapor treatment significantly increased the OH* content on the catalyst, and the Pt/Mn/ γ -Al₂O₃/Al-WVT-2 exhibited the highest hydroxyl content. The result matches the OH* distribution analyzed in the O 1s of XPS.

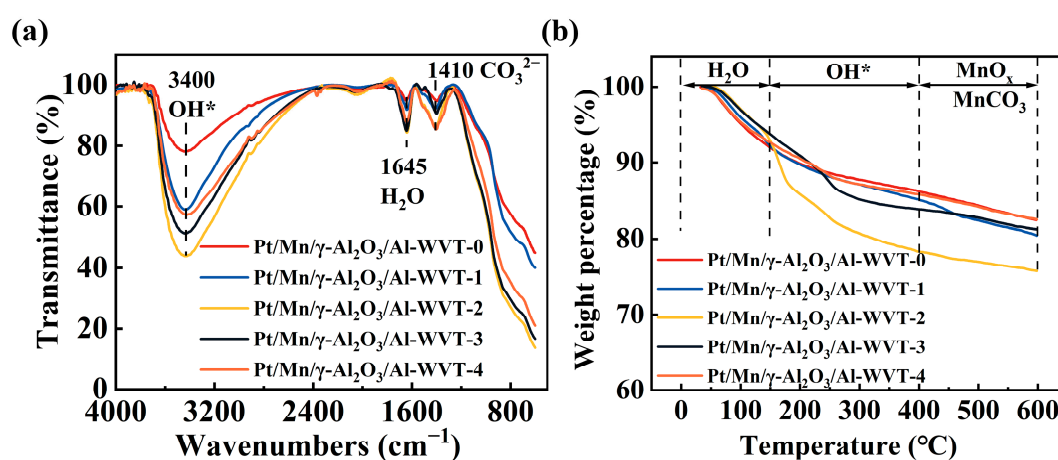


Figure 8. FTIR spectra (a) and TG curves (b) of Pt/Mn/ γ -Al₂O₃/Al-WVT-X catalysts (X = 0, 1, 2, 3, and 4).

To verify that Mn modification could effectively enhance the dissociation of H₂O into OH* and subsequently improve both activity and durability, CO catalytic oxidation tests were conducted on Pt/ γ -Al₂O₃/Al-WVT-X, Mn/ γ -Al₂O₃/Al-WVT-X, and Pt/Mn/ γ -Al₂O₃/Al-WVT-X. As shown in Figure 9a, the CO catalytic activity of Pt/ γ -Al₂O₃/Al decreased conversely following the water vapor treatment. However, as shown in Figure 9b, the catalytic oxidation activity of CO on Mn/ γ -Al₂O₃/Al slightly increased with increasing treatment time. Although the Mn/ γ -Al₂O₃/Al showed limited activity in CO catalytic oxidation, it created a hydroxyl-rich environment that slightly improved catalytic performance. This improvement aligns with the lower dissociation energy barrier of MnO₂ predicted by DFT calculations. Figure 9c shows the CO catalytic oxidation performance of Pt/Mn/ γ -Al₂O₃/Al. The average CO conversion for Pt/Mn/ γ -Al₂O₃/Al-WVT-0 was 73% over 70 min, demonstrating poor activity and durability. After 18-h testing, the activity declined to 22%, as illustrated in Figure 9d. Additionally, with the increase in water vapor treatment time, the catalytic performance increased and then decreased, and the conversion was 100% of Pt/Mn/ γ -Al₂O₃/Al-WVT-2. Furthermore, the catalyst demonstrated a lifespan of 200 h at room temperature. Figure S1 shows the performance results of the Pt/Mn/ γ -Al₂O₃/Al-WVT-2 catalyst under varying humidity conditions. The catalyst was first switched from dry conditions to 30% relative humidity (RH) and then further adjusted to 50% RH. The results demonstrated that the catalyst maintained 100% CO conversion for 10 h under both humidity conditions. This phenomenon suggested that the catalyst exhibited effective catalytic performance at low relative humidity.

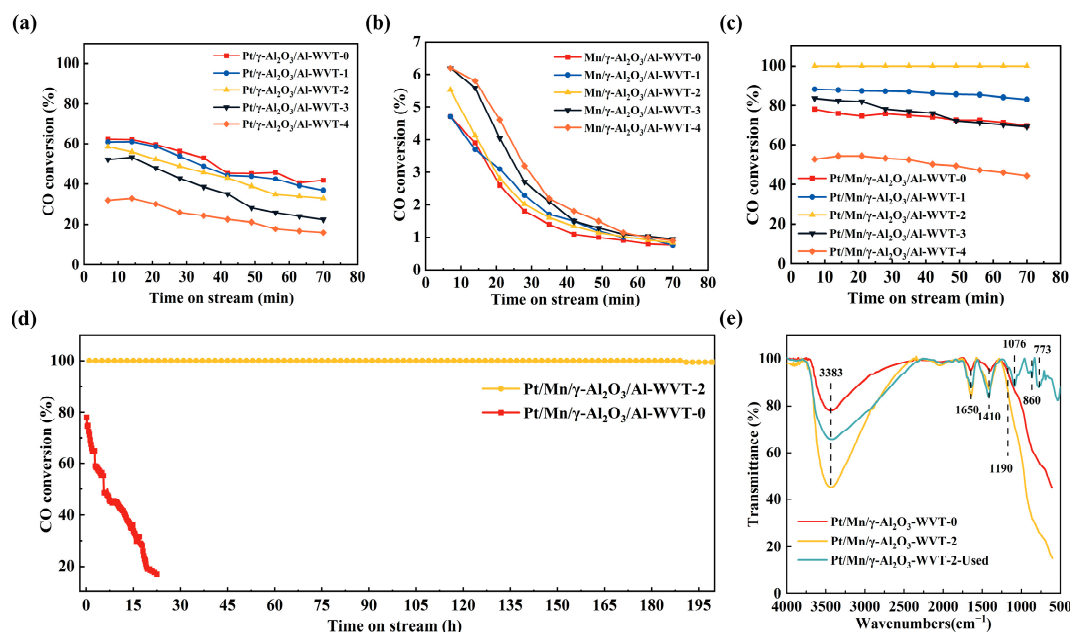


Figure 9. Activation performance of Pt/ γ -Al₂O₃/Al-WVT-X catalysts (a), Mn/ γ -Al₂O₃/Al-WVT-X catalysts (b) and Pt/Mn/ γ -Al₂O₃/Al-WVT-X catalysts (c); durability evaluation results of Pt/Mn/ γ -Al₂O₃/Al-WVT-0 and Pt/Mn/ γ -Al₂O₃/Al-WVT-2 (d); FTIR spectra of Pt/Mn/ γ -Al₂O₃/Al-0, Pt/Mn/ γ -Al₂O₃/Al-WVT-2 and Pt/Mn/ γ -Al₂O₃/Al-WVT-2-Used catalyst (e). (Condition: T = 25 ± 2 °C, m = 0.58 g, CO = 1000 ppm, WHSV = 26,000 mL·g_{cat}^{−1}·h^{−1}).

The reasons for this phenomenon have also been explored. In Figure 9e, within the range of 3100 cm^{−1} to 3700 cm^{−1}, the peak intensity of the Pt/Mn/ γ -Al₂O₃/Al-WVT-2-used catalyst was reduced. This reduction indicated that OH* was one of the key active species in the reaction, and the reaction was accompanied by the consumption of OH*. After a 200-h CO catalytic test, the OH* content of the Pt/Mn/ γ -Al₂O₃/Al-WVT-2-Used remained significantly higher than that of the untreated catalyst, suggesting that the water vapor treatment strategy successfully generated OH* on the catalyst surface. This phenomenon explained that Pt/Mn/ γ -Al₂O₃/Al-WVT-2 formed a self-sustaining cycle, which effectively delayed the OH* consumption and prolonged the durability of CO catalytic oxidation. Furthermore, FTIR peaks at 1410, 1080, 860, and 773 cm^{−1} indicated the presence of carbonates, while the weak peak at 1190 cm^{−1} suggested minor formate accumulation on the surface of the Pt/Mn/ γ -Al₂O₃/Al-WVT-2-used [42]. The catalyst surface was mainly the accumulation of carbonates. The reaction process involved the consumption of OH*, which further indicated the formation of HCOO* on the catalyst. However, the minimal accumulation of HCOO* suggested that formate species readily reacted off on the catalyst surface. An increased accumulation of carbonates on the catalyst surface was observed, consistent with previous reports [13] demonstrating that formates are more easily oxidized than carbonates at room temperature. Therefore, it was inferred that the role of OH* was mainly to promote the CO oxidation reaction path in which the intermediate product is HCOO* and reduce the activation energy of the reaction. The experimental results align with the dissociation energy barrier of water molecules on metal atoms in DFT calculations. In the hydroxyl-rich environment, the consumption rate of OH* on the catalyst surface was significantly reduced, which was crucial for enhancing the durability of the catalyst during the CO catalytic reaction. Specifically, the abundant supply of OH* can continuously supplement the OH* consumed in the catalytic process, thereby slowing down the deactivation of the active sites of the catalyst and maintaining the long-term stability and activity of the catalyst.

2.4. Mechanism of Water Vapor Treatment and CO Oxidation Reaction

The EPR analysis was employed to verify the presence of oxygen vacancies, and the content of oxygen vacancies in Pt/Mn/ γ -Al₂O₃/Al and Pt/ γ -Al₂O₃/Al was further compared. As shown in Figure 10a, both catalysts show a symmetric signal with a g value of 2.003, indicating the presence of oxygen vacancies [38]. The peak intensity of Pt/Mn/ γ -Al₂O₃/Al was stronger than that of Pt/ γ -Al₂O₃/Al, suggesting a higher oxygen vacancies content on the surface of Pt/Mn/ γ -Al₂O₃/Al. This result is consistent with the XPS in Figure S2, where the (O_{ads} + O_{wat}) content of Pt/Mn/ γ -Al₂O₃/Al is 6% higher than that of Pt/ γ -Al₂O₃/Al. The hydroxyl group and adsorbed water molecules are usually produced on oxygen vacancies of MnO₂ [38]; the increased proportion of (O_{ads} + O_{wat}) suggested more oxygen vacancies content on Pt/Mn/ γ -Al₂O₃/Al.

To explore the adsorption state of H₂O on the Pt/Mn/ γ -Al₂O₃/Al catalyst surface, in situ FTIR H₂O adsorption experiments were carried out. As shown in Figure 10b, the color gradient (from blue to red) illustrates the real-time evolution of the catalyst under H₂O/Ar gas flow throughout the 60-min test, with data points collected at 5-min intervals. The blue curve corresponds to the initial state (0 min), while the red curve represents the final state after 60 min of reaction. With the extension of the water vapor purging time, the peak intensities at 1640 cm⁻¹ and 3383 cm⁻¹ showed a gradually increasing trend. There was obvious H₂O adsorption and hydroxyl generation on the surface of the Pt/Mn/ γ -Al₂O₃/Al catalyst. Furthermore, this experiment proved that H₂O could dissociate on the surface of the catalyst without the participation of oxygen. This finding is consistent with the results of isotope-labeling experiments reported in the literature [43], indicating no isotopic exchange between H₂O and O₂ during the dissociation of H₂O.

In situ FTIR CO adsorption saturation experiments were carried out to explore the adsorption state of CO on the catalyst surface. Figure 10c,d (red curve) shows that after 30 min of purging with a 1% CO and air mixture (CO adsorption-saturated state), catalysts were tested under an Ar gas flow. The peaks at 2360 cm⁻¹ and 2337 cm⁻¹ correspond to gas-phase bands of CO₂ adsorption [44]. The CO vibrational frequencies at 2170 cm⁻¹ and 2112 cm⁻¹ correspond to CO molecules linearly adsorbed on Pt⁰ and ionic Pt [45]. After switching to Ar purging, the intensity of the CO and CO₂ peaks for the Pt/ γ -Al₂O₃/Al gradually weakened and completely disappeared after 5 min. The corresponding peak of Pt/Mn/ γ -Al₂O₃/Al continued to disappear until the seventh minute. The comparison revealed that Mn modification significantly enhanced the CO adsorption capacity of the catalyst, leading to improved CO oxidation performance. This phenomenon aligns with the DFT calculation results. It should be noted that while Mn modification enhanced CO adsorption, short-term inert gas purging could desorb CO. This observation suggested that Mn modification did not cause excessive CO adsorption and thus would not lead to catalyst deactivation.

To further demonstrate the promoted effect of the water vapor treatment method on the catalytic reaction of the catalysts, in situ FTIR tests of Pt/Mn/ γ -Al₂O₃/Al-WVT-0 and Pt/Mn/ γ -Al₂O₃/Al-WVT-2 were conducted, as shown in Figure 10e,f. The in situ FTIR spectra of the two catalysts showed many similarities. As for the change trend of CO and CO₂ peaks on catalysts, these were consistent with the change trend in reference [16]. When the CO reaction gas entered the system, the catalyst would convert CO to CO₂, resulting in the accumulation of adsorbed CO₂ on the catalyst surface. The peaks of 3383 cm⁻¹ decreased significantly during the CO catalytic reaction, indicating that the reaction process was accompanied by the depletion of OH*. This was consistent with the results of the FTIR spectra in Figure 9e, that is, Pt/Mn/ γ -Al₂O₃/Al-WVT-2 after the 200 h test, and the amount of OH* was significantly lower than before.

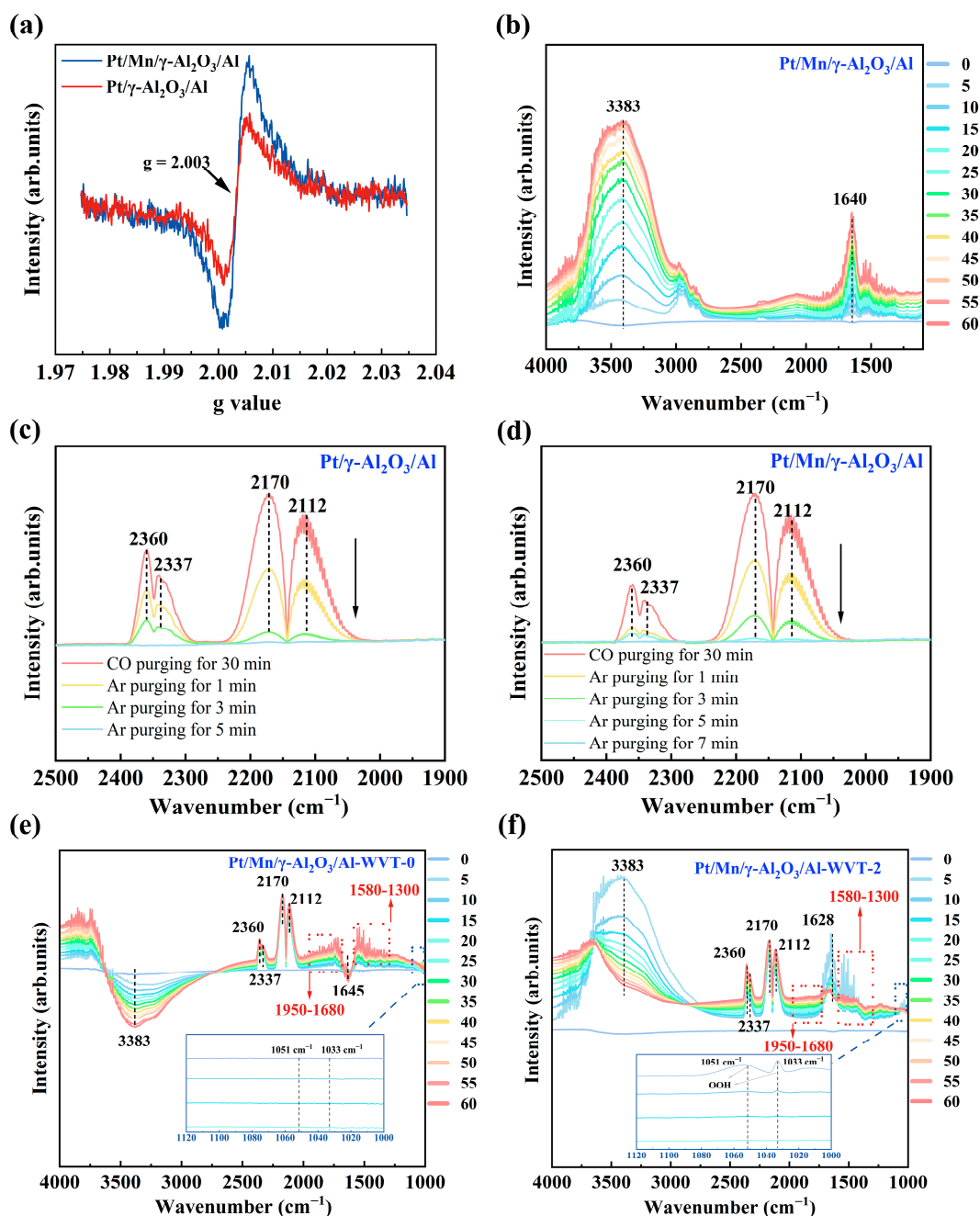


Figure 10. EPR spectra (a) of Pt/Mn/γ-Al₂O₃/Al and Pt/γ-Al₂O₃/Al; in situ FTIR spectra of Pt/Mn/γ-Al₂O₃/Al (b) under H₂O/Ar gas flow; in situ FTIR spectra of CO adsorption-saturated Pt/γ-Al₂O₃/Al (c) and Pt/Mn/γ-Al₂O₃/Al (d) under Ar gas flow; in situ FTIR spectra of Pt/Mn/γ-Al₂O₃/Al-WVT-0 (e) and Pt/Mn/γ-Al₂O₃/Al-WVT-2 (f) under 1% CO with air gas flow.

As shown in Figure 10e,f, the color gradient (from blue to red) illustrates the real-time evolution of the catalyst under 1% CO with air gas flow throughout the 60-min test, with data points collected at 5-min intervals. The blue curve corresponds to the initial state (0 min), while the red curve represents the final state after 60 min of reaction. Several distinct differences were observed in the in situ FTIR spectra of the two catalysts. One was the characteristic peaks at 1580–1300 cm⁻¹ for the Pt/Mn/γ-Al₂O₃/Al-WVT-0 corresponding to carbonates and formates [46,47]. The peak bands at 1550 cm⁻¹ together with the bands at 1360 cm⁻¹ were attributed to formates. The peak bands in the region 1460–1510 cm⁻¹, together with the bands at 1350 cm⁻¹ were assigned by carbonates. The other was the bands at 1950–1680 cm⁻¹, which corresponded to the bridge adsorption of CO on the

catalyst surface [47,48]. Bridged CO readily reacted with surface oxygen species due to the high stability and large adsorption area, facilitating the formation of carbonate species on the catalyst surface [49]. At room temperature, carbonates tended to accumulate on the catalyst surface due to their high thermodynamic stability. This result is consistent with the literature [10,50] that formates were more easily decomposed than carbonates on the catalyst surface.

Furthermore, with prolonged CO exposure, the OH* on the catalyst surface was progressively consumed while formate species accumulated. This finding proved that OH* reacted with CO* to form formate species ($\text{OH}^* + \text{CO}^* \rightarrow \text{HCOO}^*$). This observation is consistent with previously reported reaction mechanisms [37], further confirming the pathway of CO reacting with surface hydroxyl groups to form formate species. As shown in Figure 10f, it is noteworthy that no obvious accumulation of HCOO* was detected on Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al-WVT-2, indicating that the HCOO* intermediate was rapidly oxidized to CO₂. After water vapor treatment, CO oxidation primarily occurred through linear adsorption on the top sites of Pt⁰ rather than through bridged adsorption. This result further confirmed the absence of carbonate species accumulation on the catalyst surface, suggesting that the CO oxidation preferentially proceeded via the formate pathway after water vapor treatment. Moreover, within the first five min, a pair of distinct absorption peaks initially appeared at 1036 and 1051 cm⁻¹. These peaks were identified as the intermediate OOH* [51] formed by the combination of HCOO* with O₂ [13]. Subsequently, these peaks disappeared as a pair of adsorbed CO₂ vibrational bands emerged. No OOH* absorption peaks were observed on Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al-WVT-0 surface, indicating that Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al-WVT-0 mainly followed the carbonate paths.

In conclusion, there were two primary reaction pathways for the CO catalytic reaction on these catalysts. The first pathway involved CO* reacting with oxygen species to form intermediate carbonates (carbonate pathway), where bridge-adsorbed CO* reacts with surface oxygen to generate carbonate intermediates. The weak desorption capacity of carbonates at room temperature led to carbonate accumulation on the surface. The second pathway involved CO* reacting with OH* on the catalyst surface to produce formate (formate pathway). Furthermore, the HCOO* intermediate reacted with O₂* to form OOH*, which subsequently facilitated the combination of HCOO* with another CO*, leading to decarboxylation and the release of CO₂ through electron transfer. This observation aligns with previous reports in the literature [50].

The kinetic data (Arrhenius plots) were analyzed to further reveal the inherent catalytic activity of CO oxidation over the catalysts, as shown in Figure 11. The apparent energy activation (E_a) Pt was 45.4 kJ·mol⁻¹. Following Mn modification, the E_a of Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al-WVT-0 was decreased to 27.0 kJ·mol⁻¹. Moreover, after proper water vapor treatment, the E_a of Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al-WVT-2 was reduced to only 14.0 kJ·mol⁻¹. These results suggested that the enhancement of intrinsic activity toward CO oxidation on Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al-WVT-2 was primarily attributed to the Mn-modification and the amount of OH*.

It was found that Mn modification significantly increased the specific surface area of the catalyst. Materials with a high specific surface area are more likely to form defects and generate abundant oxygen vacancies [52]. XPS and EPR characterization results confirmed that the introduction of Mn³⁺ was accompanied by the formation of abundant oxygen vacancies [53]. Consequently, Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3$ /Al possessed more oxygen vacancies than Pt/ $\gamma\text{-Al}_2\text{O}_3$ /Al. These oxygen vacancies readily captured H₂O, while Mn³⁺ on the surface easily released electrons. This synergistic effect promoted the adsorption of H₂O on the catalyst surface and facilitated O–H bond cleavage. As a result, H₂O adsorbed on the MnO₂ surface readily dissociates to form OH*.

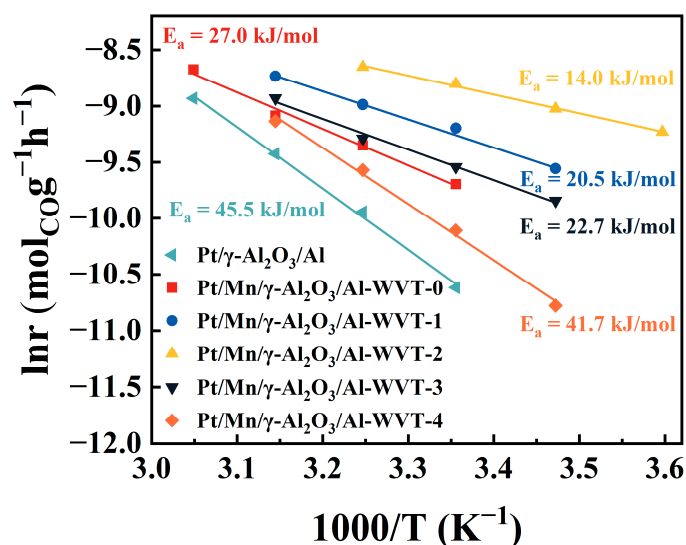
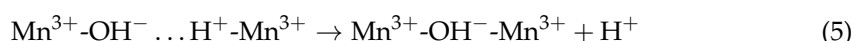
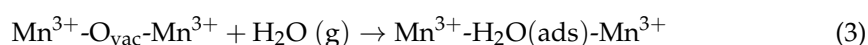


Figure 11. Arrhenius plots of all catalysts for CO oxidation. (Conditions: 23 mg catalyst, WHSV = 260,000 mL_{cat}^{−1}·h^{−1}, 1000 ppm CO with air balance).

It was reported [54] that Pt-based catalysts with different carriers (Fe₂O₃, ZnO, and γ-Al₂O₃) exhibited superior CO oxidation catalytic activity due to increased hydroxyl content. Meanwhile, as shown in Figure 9b, Mn/γ-Al₂O₃/Al showed almost no activity in CO catalytic oxidation. Combined with in situ FTIR results, CO was first linearly adsorbed by Pt atoms on the catalyst in the catalytic oxidation. It can be considered that Pt in this study provided the main active sites. The CO reaction process in the proposed mechanism diagram was on the Pt atoms. TG, FTIR, and XPS results showed that the improved activity and durability could be attributed to the increase in OH* content. The presence of abundant OH* directs the catalyst to favor the formate pathway over the carbonate pathway. Since formate demonstrates higher decomposition efficiency than carbonate at room temperature, thereby improving the reaction performance.

The DFT calculations reported in the literature [55] revealed that H₂O preferentially adsorbed on the Mn³⁺ species of defective facets, resulting in the separation of electrons (e[−]) and holes (h⁺) from the surface of MnO₂. During this step, adsorbed H₂O accepted holes (h⁺) to form OH* species, thereby releasing H⁺ species. Based on the above analysis, a mechanism for the water vapor treatment stage has been proposed, as shown in the left side of Figure 12. The Mn³⁺ site readily adsorbed water molecules through oxygen vacancies (O_{vac}) (Equation (3)). The high-spin 3d⁴ electron configuration of Mn³⁺ could donate multiple free electrons [30,56], and then the O–H bond of H₂O at the oxygen vacancies was broken, and H⁺ was released [57] (Equation (4)). The OH* remained on the MnO_x to further promote the catalytic reaction of CO (Equation (5)).



As shown on the right side of Figure 12, a mechanism of OH-promoted formate pathway was proposed. CO was easily linearly adsorbed at the top site of Pt⁰ with an adsorption energy of −3.14 eV (I → II, Figure 12). The combination of CO and OH* would generate the intermediate product HCOO* (II → III, Figure 12). Subsequently, HCOO* would be oxidized to OOH* by active oxygen, and CO₂ would be removed by deprotonation (IV → V, Figure 12). This corresponds to the results observed in Figure 10f. Subsequently, another CO molecule

was linearly adsorbed and reacted with OOH^* (VI $\rightarrow$ VII, Figure 12). Finally, the CO_2 on the catalyst surface was released, and OH^* was regenerated (VII $\rightarrow$ I, Figure 12). This mechanism aligns with earlier studies [14]. During the catalyst reaction cycles, Mn-modification was beneficial to resist the consumption of OH^* on the catalyst surface. The enhanced formate pathway further facilitated the in situ generation of OH^* and promoted a self-circulation of CO catalytic reaction.

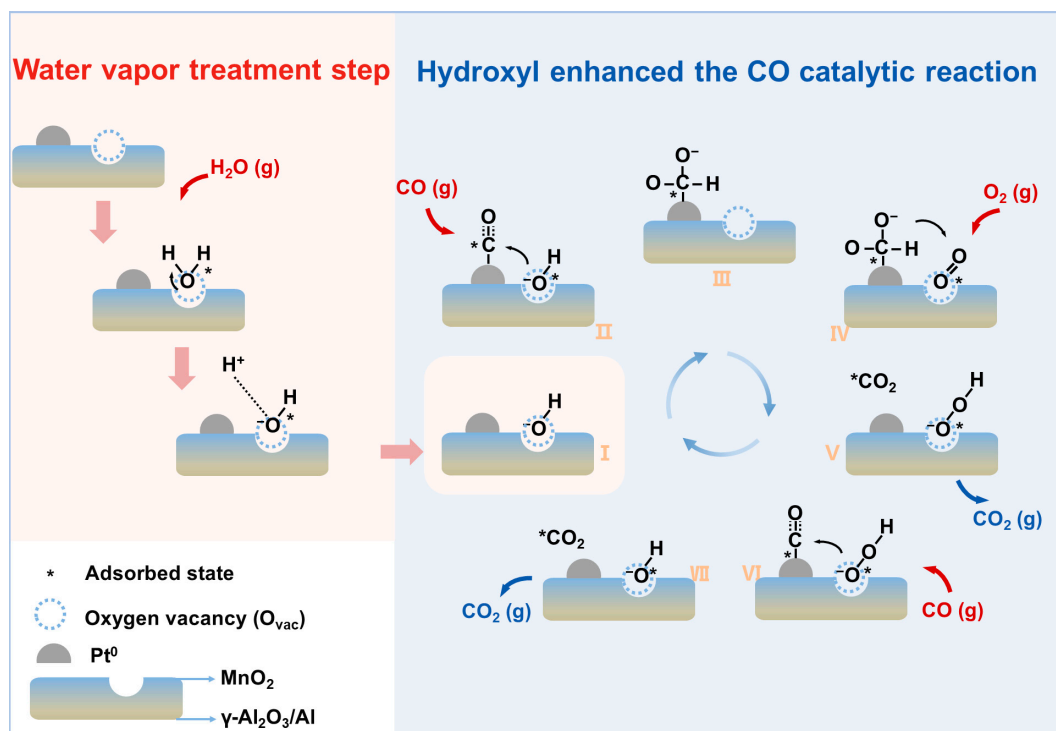


Figure 12. Proposed mechanism of water vapor treatment and the CO oxidation on Pt–MnO₂ with OH* interface.

3. Materials and Methods

3.1. Catalyst Preparation

All chemicals used in catalyst preparation were of analytical grade. In this study, the mesh-type structured carrier $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ was developed by the anodizing method [23]. MnO_x was developed by the co-precipitation method, while Pt was developed by the colloidal precipitation method following Mn modification. The detailed preparation methods for the carrier and catalysts are provided in Supplementary Notes S1–S3.

For the water vapor treatment method, $30\text{ mL}\cdot\text{min}^{-1}$ high-purity air was passed through a bubbler filled with deionized water and introduced into a quartz tube containing Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ in the form of water vapor. The samples were exposed to water vapor for 0 h (untreated), 1 h, 2 h, 3 h, and 4 h. These samples were designated as Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ -WVT-X, where X indicated the water vapor treatment time. For the sake of convenience, Pt/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ -WVT-0 and Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ -WVT-0 were simplified to Pt/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ and Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$. In addition, Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ -WVT-2-used denotes the Pt/Mn/ $\gamma\text{-Al}_2\text{O}_3/\text{Al}$ -WVT-2 after a 200-h CO catalytic reaction test.

3.2. Catalyst Characterization

The detailed characterization methods for catalysts are shown in Supplementary Note S4.

3.3. Catalytic Activity Evaluation

The catalytic activity evaluation methods are detailed in Supplementary Note S5. The flowchart of the experimental device used for the CO catalytic oxidation reaction is illustrated in Figure S3.

3.4. DFT Method

The detailed DFT methods for catalysts are presented in Supplementary Note S6.

4. Conclusions

In this work, a novel mesh-type structured Pt/Mn/ γ -Al₂O₃/Al catalyst capable of dissociating H₂O to OH* was developed. A new strategy of water vapor treatment was employed to generate OH* in situ. This method effectively produced a catalyst Pt/Mn/ γ -Al₂O₃/Al-WVT-2 with the ability to capture OH*, which solved the problem of poor activity and short durability of the catalyst. The reasons for the excellent activity and prolonged lifespan of the Pt/Mn/ γ -Al₂O₃/Al-WVT-2 are as follows:

(1) According to the DFT calculations, Mn-modification enhanced the adsorption capacity of CO and reduced both the work function and the energy barrier of the catalytic reaction. Additionally, the water molecule dissociation ability of the Pt catalyst was improved due to the Mn-modification.

(2) The preferred Pt/Mn/ γ -Al₂O₃/Al exhibited a large specific surface area and pore volume, which enhanced the activity of the Pt-based catalyst. Moreover, the XRD results suggested that the Mn-modification could improve the dispersion of Pt particles on the carrier surface.

(3) Mn³⁺ provided the adsorption sites for H₂O and facilitated the breaking of the O–H bond, enabling the adsorbed H₂O on the MnO₂ surface to readily dissociate and generate OH* in situ.

(4) Formate decomposed more readily than carbonates on the catalyst surface. In the presence of abundant OH*, CO oxidation intermediates were more likely to generate HCOO* species.

(5) Water vapor treatment facilitated CO reaction with OH* to form formates, which readily underwent oxidative decomposition on the catalyst surface. Therefore, the catalyst achieved self-circulation through the abundant presence of OH* during the reaction, thereby enhancing the durability of the catalyst.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15050430/s1>. Note S1: Preparation of flexible mesh-type γ -Al₂O₃/Al carrier, Note S2: Preparation of Mn_x/ γ -Al₂O₃/Al catalysts, Note S3: Preparation of Pt-based catalyst, Note S4: Catalyst characterization, Note S5: Catalytic activity evaluation, Note S6: DFT method, Figure S1: Activity performance of Pt/Mn/ γ -Al₂O₃/Al-WVT-2 under different relative humidity (RH). (Condition: T = 25 ± 2 °C, m = 0.58 g, CO = 1000 ppm, WHSV = 26,000 mL·g_{cat}^{−1}·h^{−1}), Figure S2: XPS O 1s results of Pt/Mn/ γ -Al₂O₃/Al and Pt/ γ -Al₂O₃/Al, Figure S3: Flowchart of experiment device for CO catalytic oxidation reaction. Refs. [58,59] are cited in the Supplementary Materials.

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References

1. Miller, S.M.; Matross, D.M.; Andrews, A.E.; Millet, D.B.; Longo, M.; Gottlieb, E.W.; Hirsch, A.I.; Gerbig, C.; Lin, J.C.; Daube, B.C.; et al. Sources of Carbon Monoxide and Formaldehyde in North America Determined from High-Resolution Atmospheric Data. *Atmos. Chem. Phys.* **2008**, *8*, 7673–7696. [\[CrossRef\]](#)
2. Wang, Y.; Yuan, Q.; Li, T.; Zhu, L. Global Spatiotemporal Estimation of Daily High-Resolution Surface Carbon Monoxide Concentrations Using Deep Forest. *J. Clean. Prod.* **2022**, *350*, 131500. [\[CrossRef\]](#)
3. Dent, M.R.; Rose, J.J.; Tejero, J.; Gladwin, M.T. Carbon Monoxide Poisoning: From Microbes to Therapeutics. *Annu. Rev. Med.* **2024**, *75*, 337–351. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Jing, P.; Gong, X.; Liu, B.; Zhang, J. Recent Advances in Synergistic Effect Promoted Catalysts for Preferential Oxidation of Carbon Monoxide. *Catal. Sci. Technol.* **2020**, *10*, 919–934. [\[CrossRef\]](#)
5. Rao, R.; Sun, H.; Dong, X.; Dong, H.; Fang, W.; Tang, Y.; Fang, S.; Hu, C. A Facile and Large-Scale Synthesis of Co₃O₄/N-Doped Graphene for CO Oxidation: Low-Temperature Catalytic Activity and the Role of Nitrogen States. *Appl. Surf. Sci.* **2020**, *513*, 145800. [\[CrossRef\]](#)
6. Boronin, A.I.; Slavinskaya, E.M.; Figueroba, A.; Stadnichenko, A.I.; Kardash, T.Y.; Stonkus, O.A.; Fedorova, E.A.; Muravev, V.V.; Svetlichnyi, V.A.; Bruix, A.; et al. CO Oxidation Activity of Pt/CeO₂ Catalysts below 0 Degrees C: Platinum Loading Effects. *Appl. Catal. B-Environ.* **2021**, *286*, 119931. [\[CrossRef\]](#)
7. Luo, Y.; He, T.; Li, G.; Wu, D.; Liu, W.; Zhang, S.; Peng, H. Synthetic Pt-Fe(OH)_x Catalysts by One-Pot Method for CO Catalytic Oxidation. *Front. Chem.* **2024**, *12*, 1413489. [\[CrossRef\]](#)
8. Zhang, T.; Zheng, P.; Gao, J.; Liu, X.; Ji, Y.; Tian, J.; Zou, Y.; Sun, Z.; Hu, Q.; Chen, G.; et al. Simultaneously Activating Molecular Oxygen and Surface Lattice Oxygen on Pt/TiO₂ for Low-Temperature CO Oxidation. *Nat. Commun.* **2024**, *15*, 6827. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Wang, T.; Xing, J.-Y.; Jia, A.-P.; Tang, C.; Wang, Y.-J.; Luo, M.-F.; Lu, J.-Q. CO Oxidation over Pt/Cr_{1.3}Fe_{0.7}O₃ Catalysts: Enhanced Activity on Single Pt Atom by H₂O Promotion. *J. Catal.* **2020**, *382*, 192–203. [\[CrossRef\]](#)
10. Li, J.-J.; Zhu, B.-L.; Wang, G.-C.; Liu, Z.-F.; Huang, W.-P.; Zhang, S.-M. Enhanced CO Catalytic Oxidation over an Au–Pt Alloy Supported on TiO₂ Nanotubes: Investigation of the Hydroxyl and Au/Pt Ratio Influences. *Catal. Sci. Technol.* **2018**, *8*, 6109–6122. [\[CrossRef\]](#)
11. Zhang, N.; Li, L.; Wu, R.; Song, L.; Zheng, L.; Zhang, G.; He, H. Activity Enhancement of Pt/MnO_x Catalyst by Novel β-MnO₂ for Low-Temperature CO Oxidation: Study of the CO–O₂ Competitive Adsorption and Active Oxygen Species. *Catal. Sci. Technol.* **2019**, *9*, 347–354. [\[CrossRef\]](#)
12. Deng, Y.; Liu, S.; Fu, L.; Yuan, Y.; Zhao, A.; Wang, D.; Zheng, H.; Ouyang, L.; Yuan, S. Crystal Plane Induced Metal-Support Interaction in Pd/Pr-CeO₂ Catalyst Boosts H₂O-Assisted CO Oxidation. *J. Catal.* **2023**, *417*, 60–73. [\[CrossRef\]](#)
13. Lin, J.; Zhao, S.; Yang, J.; Huang, W.-H.; Chen, C.-L.; Chen, T.; Zhao, Y.; Chen, G.; Qiu, Y.; Gu, L. Hydrogen Spillover Induced PtCo/CoO_x Interfaces with Enhanced Catalytic Activity for CO Oxidation at Low Temperatures in Humid Conditions. *Small* **2023**, *20*, 2309181. [\[CrossRef\]](#)
14. Liu, J.; Liang, Z.; Xie, Z.; Shu, Q.; Zhu, Y.; Zhang, Q. Fe-Modified Hydroxyl-Rich Structured Pt/Fe_x/γ-Al₂O₃/Al Catalyst for CO Oxidation at Room Temperature: Behavior and Mechanism. *React. Kinet. Mech. Catal.* **2023**, *136*, 1283–1299. [\[CrossRef\]](#)
15. Zhao, S.; Wen, Y.; Liu, X.; Pen, X.; Lu, F.; Gao, F.; Xie, X.; Du, C.; Yi, H.; Kang, D.; et al. Formation of Active Oxygen Species on Single-Atom Pt Catalyst and Promoted Catalytic Oxidation of Toluene. *Nano Res.* **2020**, *13*, 1544–1551. [\[CrossRef\]](#)
16. Zhang, H.; Sui, S.; Zheng, X.; Cao, R.; Zhang, P. One-Pot Synthesis of Atomically Dispersed Pt on MnO₂ for Efficient Catalytic Decomposition of Toluene at Low Temperatures. *Appl. Catal. B-Environ.* **2019**, *257*, 117878. [\[CrossRef\]](#)
17. Li, X.; Ren, S.; Chen, Z.; Jiang, Y.; Wang, M.; Wang, L.; Liu, M. Unraveling the Morphology and Crystal Plane Dependence of Bifunctional MnO₂ Catalyst for Simultaneous Removal of NO and CO at Low Temperature. *Sep. Purif. Technol.* **2023**, *325*, 124760. [\[CrossRef\]](#)
18. Li, X.; Jiang, Y.; Ren, S.; Chen, Z.; Wang, M.; Li, J.; Yang, J.; Chen, H. A Comparison of Bifunctional MnO_x Catalysts Prepared via Different Precipitants for Simultaneous Removal NO and CO. *Mol. Catal.* **2023**, *549*, 113524. [\[CrossRef\]](#)
19. Shan, R.; Sheng, Z.; Hu, S.; Xiao, H.; Zhang, Y.; Zhang, J.; Wang, L.; Zhang, C.; Li, J. Enhancing Oxidation Reaction over Pt-MnO₂ Catalyst by Activation of Surface Oxygen. *J. Environ. Sci.* **2023**, *134*, 117–125. [\[CrossRef\]](#)
20. Yan, X.; Gan, T.; Shi, S.; Du, J.; Xu, G.; Zhang, W.; Yan, W.; Zou, Y.; Liu, G. Potassium-Incorporated Manganese Oxide Enhances the Activity and Durability of Platinum Catalysts for Low-Temperature CO Oxidation. *Catal. Sci. Technol.* **2021**, *11*, 6369–6373. [\[CrossRef\]](#)
21. Wu, D.; Song, L.; Zhang, B.; Li, Y. Effect of the Mechanical Failure of Catalyst Pellets on the Pressure Drop of a Reactor. *Chem. Eng. Sci.* **2003**, *58*, 3995–4004. [\[CrossRef\]](#)

22. Zhang, W.; Xie, W.; Ma, T.; Zhang, Q. Development of Zn Doping Fe-Pd Bifunctional Mesh-Type Catalyst for Heterogeneous Electro-Fenton System. *AIChE J.* **2025**, *71*, e18604. [\[CrossRef\]](#)
23. Zhang, Q.; Luan, H.; Li, T.; Wu, Y.; Ni, Y. Study on Pt-Structured Anodic Alumina Catalysts for Catalytic Combustion of Toluene: Effects of Competitive Adsorbents and Competitive Impregnation Methods. *Appl. Surf. Sci.* **2016**, *360*, 1066–1074. [\[CrossRef\]](#)
24. Li, R.; Zheng, X.; Yan, H.; Tuo, Y.; Liu, Y.; Feng, X.; Chen, X.; Chen, D.; Yang, C. Understanding the Promotion Effect of Pt in the Reaction System of Water Gas Shift Reaction Catalyzed by Pt/ α -MoC from Theoretical Perspectives. *Appl. Surf. Sci.* **2024**, *644*, 158800. [\[CrossRef\]](#)
25. Wang, A.; Wu, Y.; Shen, X.; Zhang, Q.; Jian, H.; Han, C. Efficient Ozone Decomposition by Amorphous Mn-Ni Bimetallic Catalysts under an Entire Humidity Environment. *J. Environ. Chem. Eng.* **2024**, *12*, 113848. [\[CrossRef\]](#)
26. Zhang, Q.; Fan, F.; Xu, G.; Ye, D.; Wang, W.; Zhu, Z. Steam Reforming of Dimethyl Ether over a Novel Anodic γ -Al₂O₃ Supported Copper Bi-Functional Catalyst. *Int. J. Hydrogen Energy* **2013**, *38*, 10305–10314. [\[CrossRef\]](#)
27. Zhang, Q.; Sun, D.; Fan, F.; Zhang, Q.; Zhu, Z. A Novel Monolith Catalyst of Plate-Type Anodic Alumina for the Hydrolysis of Dimethyl Ether. *Catal. Commun.* **2013**, *34*, 64–68. [\[CrossRef\]](#)
28. Lü, H.; Gao, J.; Jiang, Z.; Jing, F.; Yang, Y.; Wang, G.; Li, C. Ultra-Deep Desulfurization of Diesel by Selective Oxidation with [C₁₈H₃₇N(CH₃)₃]₄[H₂NaPW₁₀O₃₆] Catalyst Assembled in Emulsion Droplets. *J. Catal.* **2006**, *239*, 369–375. [\[CrossRef\]](#)
29. Zhu, L.; Wang, J.; Rong, S.; Wang, H.; Zhang, P. Cerium Modified Birnessite-Type MnO₂ for Gaseous Formaldehyde Oxidation at Low Temperature. *Appl. Catal. B Environ.* **2017**, *211*, 212–221. [\[CrossRef\]](#)
30. Liu, X.; Wu, J.; Zhang, S.; Li, Q.; Wu, Z.; Zhang, J. Evaluation of an ϵ -Manganese (IV) Oxide/Manganese Vanadium Oxide Composite Catalyst Enriched with Oxygen Vacancies for Enhanced Formaldehyde Removal. *Appl. Catal. B Environ.* **2023**, *320*, 121994. [\[CrossRef\]](#)
31. Shu, Q.; Xiang, Y.; Zhang, Q. Planar Growth, Facet-Oriented La₂O₃ (003) in CuLa Catalysts: Enhancement in Charge Transport and Water Adsorption for Methanol Steam Reforming. *Fuel* **2025**, *381*, 133612. [\[CrossRef\]](#)
32. Muravev, V.; Parastayev, A.; van den Bosch, Y.; Ligt, B.; Claes, N.; Bals, S.; Kosinov, N.; Hensen, E.J.M. Size of Cerium Dioxide Support Nanocrystals Dictates Reactivity of Highly Dispersed Palladium Catalysts. *Science* **2023**, *380*, 1174–1179. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Liang, L.; Jin, H.; Zhou, H.; Liu, B.; Hu, C.; Chen, D.; Wang, Z.; Hu, Z.; Zhao, Y.; Li, H.-W.; et al. Cobalt Single Atom Site Isolated Pt Nanoparticles for Efficient ORR and HER in Acid Media. *Nano Energy* **2021**, *88*, 106221. [\[CrossRef\]](#)
34. Ma, C.; Pan, J.; Chen, C.; Dong, Y.; Yao, F.; Wang, F.; Song, M. Investigation into the Roles of Interfacial H₂O Structure in Catalytic Oxidation of HCHO and CO over CuMnO₂ Catalysts. *J. Environ. Sci.* **2024**, *137*, 310–320. [\[CrossRef\]](#)
35. Lizarbe, A.J.; Major, G.H.; Fernandez, V.; Fairley, N.; Linford, M.R. Insight Note: X-Ray Photoelectron Spectroscopy (XPS) Peak Fitting of the Al_{2p} Peak from Electrically Isolated Aluminum Foil with an Oxide Layer. *Surf. Interface Anal.* **2023**, *55*, 651–657. [\[CrossRef\]](#)
36. Ma, L.; Ding, C.; Ma, Z.; Wang, J.; Xu, H.; Zhang, K.; Li, G. Defect Engineering by Steam Treatment over Pt/CeO₂ Catalyst Promoting C–H Activation in Partial Oxidation of Methane. *Int. J. Hydrogen Energy* **2023**, *48*, 17055–17064. [\[CrossRef\]](#)
37. Chen, Y.; Feng, Y.; Li, L. Identification of Active Sites on High-Performance Pt/Al₂O₃ Catalyst for Cryogenic CO Oxidation. Available online: <https://pubs.acs.org/doi/epdf/10.1021/acscatal.0c02253> (accessed on 5 September 2023).
38. Xie, Z.; Ji, L.; Bian, H.; Zhang, Q. Generation of Abundant Oxygen Vacancies in Sandwich Structured ϵ -MnO₂/ γ -Al₂O₃/Al by a Facile Modification Strategy for Enhanced Catalytic Decomposition of Ozone in Humid Conditions. *Chem. Eng. J.* **2025**, *509*, 161202. [\[CrossRef\]](#)
39. Li, H.; Xu, S.; Du, J.; Tang, J.; Zhou, Q. Cu@Co-MOFs as a Novel Catalyst of Peroxymonosulfate for the Efficient Removal of Methylene Blue. *RSC Adv.* **2019**, *9*, 9410–9420. [\[CrossRef\]](#)
40. Ma, C.; Yang, C.; Wang, B.; Chen, C.; Wang, F.; Yao, X.; Song, M. Effects of H₂O on HCHO and CO Oxidation at Room-Temperature Catalyzed by MCo₂O₄ (M=Mn, Ce and Cu) Materials. *Appl. Catal. B Environ.* **2019**, *254*, 76–85. [\[CrossRef\]](#)
41. Merin Saju, S.; Vargeese, A.A. Synthesis of Perforated Single-Crystalline Mn₂O₃ Microcubes for Thermocatalytic Applications. *New J. Chem.* **2024**, *48*, 17150–17158. [\[CrossRef\]](#)
42. Meunier, F.C.; Reid, D.; Goguet, A.; Shekhtman, S.; Hardacre, C.; Burch, R.; Deng, W.; Flytzani-Stephanopoulos, M. Quantitative Analysis of the Reactivity of Formate Species Seen by DRIFTS over a Au/Ce(La)O₂ Water–Gas Shift Catalyst: First Unambiguous Evidence of the Minority Role of Formates as Reaction Intermediates. *J. Catal.* **2007**, *247*, 277–287. [\[CrossRef\]](#)
43. Chen, G.; Zhao, Y.; Fu, G.; Duchesne, P.N.; Gu, L.; Zheng, Y.; Weng, X.; Chen, M.; Zhang, P.; Pao, C.-W.; et al. Interfacial Effects in Iron-Nickel Hydroxide-Platinum Nanoparticles Enhance Catalytic Oxidation. *Science* **2014**, *344*, 495–499. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Pereira-Hernández, X.I.; DeLaRiva, A.; Muravev, V.; Kunwar, D.; Xiong, H.; Sudduth, B.; Engelhard, M.; Kovarik, L.; Hensen, E.J.M.; Wang, Y.; et al. Tuning Pt-CeO₂ Interactions by High-Temperature Vapor-Phase Synthesis for Improved Reducibility of Lattice Oxygen. *Nat. Commun.* **2019**, *10*, 1358. [\[CrossRef\]](#)
45. Ogihara, Y.; Yano, H.; Matsumoto, T.; Tryk, D.A.; Iiyama, A.; Uchida, H. In Situ FTIR Analysis of CO-Tolerance of a Pt-Fe Alloy with Stabilized Pt Skin Layers as a Hydrogen Anode Catalyst for Polymer Electrolyte Fuel Cells. *Catalysts* **2017**, *7*, 8. [\[CrossRef\]](#)

46. Zhang, Z.; Xu, J.; Kang, J.; Chen, Y. Role of Bridge-bonded Formate in Formic Acid Dehydration to CO at Pt Electrode: Electrochemical In-situ Infrared Spectroscopic Study. *Chin. J. Chem. Phys.* **2013**, *26*, 471–476. [\[CrossRef\]](#)
47. Zhang, C.; He, H.; Tanaka, K. Catalytic Performance and Mechanism of a Pt/TiO₂ Catalyst for the Oxidation of Formaldehyde at Room Temperature. *Appl. Catal. B-Environ.* **2006**, *65*, 37–43. [\[CrossRef\]](#)
48. Yajima, T.; Uchida, H.; Watanabe, M. In-Situ ATR-FTIR Spectroscopic Study of Electro-Oxidation of Methanol and Adsorbed CO at Pt–Ru Alloy. *J. Phys. Chem. B* **2004**, *108*, 2654–2659. [\[CrossRef\]](#)
49. Tou, A.; Kim, H.-H.; Einaga, H.; Teramoto, Y.; Ogata, A. Ozone-Assisted Catalysis of CO: In Situ Fourier Transform IR Evidence of the Cooperative Effect of a Bimetallic Ag-Pd Catalyst. *Chem. Eng. J.* **2019**, *355*, 380–389. [\[CrossRef\]](#)
50. Belletti, G.D.; Colombo, E.; Cabana, N.; Quaino, P.; Collins, S. Mechanistic Investigation of Methanol Oxidation on Au/TiO₂: A Combined DRIFT and DFT Study. *Top. Catal.* **2022**, *65*, 915–925. [\[CrossRef\]](#)
51. Hao, Y.; Hung, S.-F.; Zeng, W.-J.; Wang, Y.; Zhang, C.; Kuo, C.-H.; Wang, L.; Zhao, S.; Zhang, Y.; Chen, H.-Y.; et al. Switching the Oxygen Evolution Mechanism on Atomically Dispersed Ru for Enhanced Acidic Reaction Kinetics. *J. Am. Chem. Soc.* **2023**, *145*, 23659–23669. [\[CrossRef\]](#)
52. Zhu, Y.; Yang, L.; Ma, J.; Fang, Y.; Yang, J.; Chen, X.; Zheng, J.; Zhang, S.; Chen, W.; Pan, C.; et al. Rapid Ozone Decomposition over Water-Activated Monolithic MoO₃/Graphdiyne Nanowalls under High Humidity. *Angew. Chem.* **2023**, *135*, e202309158. [\[CrossRef\]](#)
53. Vayssilov, G.N.; Mihaylov, M.; Petkov, P.S.; Hadjiivanov, K.I.; Neyman, K.M. Reassignment of the Vibrational Spectra of Carbonates, Formates, and Related Surface Species on Ceria: A Combined Density Functional and Infrared Spectroscopy Investigation. *J. Phys. Chem. C* **2011**, *115*, 23435–23454. [\[CrossRef\]](#)
54. Lou, Y.; Liu, J. CO Oxidation on Metal Oxide Supported Single Pt Atoms: The Role of the Support. *Ind. Eng. Chem. Res.* **2017**, *56*, 6916–6925. [\[CrossRef\]](#)
55. Ke, Q.; Zhang, Y.; Wan, C.; Tang, J.; Li, S.; Guo, X.; Han, M.; Hamada, T.; Osman, S.M.; Kang, Y.; et al. Sunlight-Driven and Gram-Scale Vanillin Production *via* Mn-Defected γ -MnO₂ Catalyst in Aqueous Environment. *Chem. Sci.* **2024**, *15*, 5368–5375. [\[CrossRef\]](#)
56. Xu, B.; Qin, H.; Wu, X.; Sun, Y. Ozone Decomposition Mechanism at Different Structural Oxygen Vacancies on Manganese Dioxide. *J. Phys. Chem. C* **2022**, *126*, 17076–17083. [\[CrossRef\]](#)
57. Zhang, S.; Wang, K.; He, F.; Gao, X.; Fan, S.; Ma, Q.; Zhao, T.; Zhang, J. H₂O Derivatives Mediate CO Activation in Fischer-Tropsch Synthesis: A Review. *Molecules* **2023**, *28*, 5521. [\[CrossRef\]](#)
58. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50. [\[CrossRef\]](#)
59. John, P.P.; Kieron, B. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

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