Catalytic Degradation of Benzene over Nanocatalysts containing Cerium and Manganese

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A Ce–Mn composite oxide possessing a rod-like morphology (with a fixed molar ratio of Ce/Mn = 3:7) was synthesized through a hydrothermal method. Mn ions were doped into a CeO2 framework to replace Ce ions, thereby increasing the concentration of oxygen vacancies. The formation energies of O vacancies for the Ce–Mn composite oxide were calculated by applying density functional theory (DFT). The data showed that it was easier to form an O vacancy in the composite. The catalytic behavior of the Ce–Mn composite oxide for benzene degradation was researched in detail, which exhibited a higher activity than the pure phases. Based on this, the Ce–Mn composite oxide was chosen as a supporter to load PdO nanoparticles. The activity was enhanced further compared with that of the supporter alone (for the supporter, the reaction rate \( R_{\text{Ce–Mn}} = 0.68 \times 10^{-4} \text{ mol g}_{\text{cat}}^{-1} \text{ s}^{-1} \) and apparent activation energy \( E_a = 12.75 \text{ kJ mol}^{-1} \); for the supporting catalyst, \( R_{\text{Pd/Ce–Mn}} = 1.46 \times 10^{-4} \text{ mol g}_{\text{cat}}^{-1} \text{ s}^{-1} \), \( E_a = 10.91 \text{ kJ mol}^{-1} \). The corresponding catalytic mechanism was studied through in situ Raman and FTIR spectroscopy, which indicated that the process of benzene oxidation was related to different types of oxygen species existing at the surface of the catalysts.

1. Introduction

Volatile organic compounds (VOCs) have a high vapor pressure and low water solubility and are recognized as major contributors to air pollution, both directly and as precursors to ozone and photochemical smog. Among the VOCs, aromatic compounds are one of the major hazardous pollutants emitted from stationary sources. As one of the representing aromatic materials, the complete removal of benzene is often studied as a model reaction, owing to its chemical stability. At present, the most efficient methods for benzene destruction are thermal and catalytic incineration, with the latter being the most popular because it is more versatile and economical for low concentrations of organic emissions.[11, 12]

In the procession of benzene catalytic oxidation, the choice of catalyst seems particularly important. Both classes of catalysts, noble metals and transition-metal oxides, have been widely studied for the destruction of halogenated and non-halogenated compounds.[3–7] Noble-metal-based catalysts, despite their higher costs, are preferred because of their high specific activity, resistance to deactivation, and regeneration ability.[8] To minimize the consumed quantity of these noble metals, the development of catalyst materials exhibiting high activity with a small amount of noble metals is strongly desired. Additionally, rare-earth oxides have also attracted attention over the VOCs catalytic oxidation. Ceria (CeO2), as a typical rare-earth oxide, has been investigated in heterogeneous catalysis, owing to its high oxygen storage capacity. It can provide active oxygen species to ensure the catalytic reaction. More recently, CeO2-based mixed oxides were employed for the removal of VOCs and obtained satisfying results,6–10 among which, Ce–Mn composites have been studied by various researchers. CeO2–MnO2 species can be applied as heterogeneous catalysts for the abatement of contaminants in the liquid and gas phases, such as the catalytic reduction of NO and oxidation of acrylic acid and formaldehyde, which exhibit much higher catalytic activity than those of pure MnO2 and CeO2.[11–14]

In our previous work,[15] Mn was also doped or mixed with CeO2 to obtain Ce–Mn composites. Their catalytic behaviors for benzene oxidation were researched, among which, Ce0.2Mn0.8 possessed the best catalytic activity compared with other CeO2–MnO2 composite oxides. If CeO2–MnO2 composites are used as supporters to load noble metals, typically Pd or Pt spe-
cies, the catalytic behavior over benzene could be enhanced further. As we know, the CeO$_2$ phase can improve the dispersion, oxidation, and reduction of supported noble metals, hinder coke formation on the surface of catalyst, and increase the thermal resistance of the catalyst.$^{16-22}$ Therefore, the catalytic behaviors of Ce–Mn composites or supporting samples over benzene need to be researched in detail. In addition, studies of the catalytic mechanism of Ce–Mn-based catalysts for benzene degradation have been done by many research communities; however, the conclusions remains ambiguous. Moreover, few explanations of the mechanism in the view of the crystal microstructure (such as crystal defects) are available.

Therefore, we investigated the catalytic behavior of Ce–Mn-based composites through the complete catalytic oxidation of benzene, and the corresponding catalytic mechanism was also researched with the help of in situ Raman and FTIR spectroscopy. Meanwhile, density functional theory (DFT) was adopted to simulate the crystal structure of the supporter (Ce–Mn composite) and to calculate the formation energy of oxygen vacancies. The main aim of our research is to understand the microstructure elements influencing the activity of samples in order to acquire a more active catalyst.

2. Results and Discussion

2.1 Catalysts Performances

Figure 1a shows the XRD patterns of the samples in the angular range of 2$\theta$ = 20–70°. For pure MnO$_x$, the intensive and sharp diffractions at 2$\theta$ = 23.1, 32.9, 38.2, 45.3, 49.4, 55.2, and 65.8° could primarily be attributed to Mn$_3$O$_4$ (PDF# 89-4836/65-1798). The diffraction peaks at 2$\theta$ = 28.5, 33.0, 47.4, 56.4, and 59.2° in the XRD profile of pure cerium oxide clearly demonstrate the presence of cubic fluorite structure of CeO$_2$ (PDF# 81-0792). For Ce$_{0.3}$Mn$_{0.7}$ and PdO/Ce$_{0.3}$Mn$_{0.7}$ samples, the peaks corresponding to CeO$_2$ and Mn$_3$O$_4$, respectively, can be detected. However, the diffraction peak corresponding to PdO cannot be identified in the supporting sample, which may indicate that the PdO particles are dispersed homogeneously at the surface of the support and the size is too small to be detected by using XRD.

Additionally, it is worth noting that the characteristic diffraction peak of CeO$_2$ (2$\theta$ = 28.5°) in Ce$_{0.3}$Mn$_{0.7}$ is slightly shifted to higher Bragg angles values, as compared with pure CeO$_2$ (Figure 1b). As we know, the ionic radius of Mn$^{3+}$ (0.066 nm) is smaller than that of the Ce$^{4+}$ (0.1098 nm), and the incorporation of Mn$^{3+}$ into the CeO$_2$ lattice to form Ce–O–Mn solid solution would result in a remarkable decrease in the lattice parameter of CeO$_2$ in the Ce$_{0.3}$Mn$_{0.7}$. Meanwhile, the O vacancy is also easier to form to balance charge. The microstrain (\(\varepsilon\)) values of these samples were determined from line-broadening measurements on the different crystal planes by using the equation \(\varepsilon = \frac{2q}{\lambda} tan\theta\)[23] Ce$_{0.3}$Mn$_{0.7}$ has a much higher lattice strain (\(\varepsilon = 0.223\)) than CeO$_2$ (\(\varepsilon = 0.179\)), which demonstrates that the density of oxygen vacancies in Ce$_{0.3}$Mn$_{0.7}$ is larger than that in CeO$_2$. Moreover, the addition of Pd species led to a decrease in the strain of the supports (\(\varepsilon = 0.204\)), suggesting that there was a strong interaction between PdO and Ce$_{0.3}$Mn$_{0.7}$[23].

The weight contents of Ce and Mn in the support, calculated by using inductively coupled plasma (ICP) techniques, are 36.31 and 34.52%, respectively. The remaining weight (29.17%) is attributed to oxygen. Based on the ICP results, the molar ratio of Ce/Mn/O is approximately 0.3:0.7:2; therefore, the molecular formula of the support can be written as Ce$_{0.3}$Mn$_{0.7}$. The Pd loading in the catalyst is 4.64%. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations were performed for Ce$_{0.3}$Mn$_{0.7}$ and PdO/Ce$_{0.3}$Mn$_{0.7}$ to fully characterize their shapes and surface states. As shown in Figure 2a, Ce$_{0.3}$Mn$_{0.7}$, with a nanorod morphology, has an average diameter of about 10 nm and length of about 150–300 nm. For PdO/Ce$_{0.3}$Mn$_{0.7}$ (Figure 2b), the support still possesses a rod-like shape. Loaded PdO nanoparticles can clearly be distinguished, as shown with white arrows, and are dispersed homogeneously at the surface of supports, which is beneficial for interactions to form between the supporter and the active species. The size of an active species particle is about 2 nm.

To analyze the elemental distribution, high-angle annular dark-field (HAADF) mapping and atom arrangement of Ce$_{0.3}$Mn$_{0.7}$ and PdO/Ce$_{0.3}$Mn$_{0.7}$ were examined. For Ce$_{0.3}$Mn$_{0.7}$ (Figure 2c), the Ce and Mn elements were composited together homogeneously to form supports. Meanwhile, a molar ratio of Ce/Mn atom to O atom (Ce(Mn)/O = 1/2) was also observed through the atom arrangement, in which every metal atom was surrounded by two oxygen atoms, and crystal planes ([111], [220], and [200]) corresponding to CeO$_2$ could be detected. For PdO/Ce$_{0.3}$Mn$_{0.7}$, the elemental distribution of the support was almost invariable and loaded PdO particles were more easily distinguished in the HAADF image (Figure 2d). In the atom arrangement, every Pd atom was surrounded by one Mn atom and two oxygen atoms, and crystal planes ([111], [002], and [200])...
are attributed to PdO and the (111) plane belongs to the support.

The oxidation state of catalyst surface species was examined by using X-ray photoelectron spectroscopy (XPS) analysis. Figure 3 exhibits XPS patterns of Ce 3d, Mn 2p, O 1s, and Pd 3d for the samples. In the Ce 3d spectrum of the support (Figure 3a), six peaks labeled as V_0 (881.9 eV), V_1 (888.5 eV), V_2 (897.8 eV), V'_0 (900.8 eV), V'_1 (907.3 eV), and V'_2 (916.2 eV) can be identified as characteristic of Ce^{4+} 3d final states.\[24, 25\] The high binding energy (BE) doublet (V'_2/V'_2') is attributed to the final state of Ce^{4+} 3d^4f^0 O_2p^2, V_1/V'_1 originates from the state of Ce^{4+} 3d^4f^1 O_2p^1, and the V_0/V'_0 doublet corresponds to the state of Ce^{4+} 3d^4f^2 O_2p. The characteristic peaks of Ce^{3+} are also observed at 903.3/884.6 eV and 897.9/879.2 eV, labeled as U_1/U'_1 and U_0/U'_0, respectively. The amount of Ce^{3+} is estimated to be 15.6% for the support, which can be calculated by using Equation (1). Therefore, Ce species in the support exist mainly in the tetravalent oxidation state.\[26\] In addition, Ce^{3+} can induce the formation of oxygen vacancies in the material, which are essential for absorption/dissociation of oxygen molecules during the oxidation reaction.

\[
X_{Ce^{3+}} = \frac{A_{Ce^{3+}}/S_{Ce}}{\sum A_{Ce^{2+}-Ce^{4+}}/S_{Ce}} \times 100\% \tag{1}
\]

where \(X_{Ce^{3+}}\) is the percentage content of Ce^{3+}, \(A\) is the integrated area of the characteristic peak in the XPS pattern, and \(S\) is the sensitivity factor (\(S = 7.399\)).

Figure 3b presents the Mn 2p pattern of support. The BE of the Mn 2p_{3/2} component appears at 641.7 eV and that for Mn 2p_{1/2} appears at 653.3 eV. The spin-orbit splitting is \(\Delta E = 11.6\) eV and the width is 3.62 eV. Owing to the BEs of various Mn ions being very close to each other, they often overlap in the Mn 2p patterns, making the exact identification of Mn oxidation states difficult.\[27, 28\] To determine the chemical states of Mn further, the Mn 3s XPS spectra of the support were ana-
alyzed (inner picture of Figure 3b). The distance of the twin peaks in the spectra (ΔMn 3s) is about 5.22 eV for the support, which is close to the value of 5.1 eV for the standard sample of α-MnO 2. The ΔMn 3s value of MnO is about 6.3 eV, indicating that the oxidation status of Mn is predominantly tetravalent.

The O 1s XPS spectrum (Figure 3c) shows a main peak at a BE of 529.1 eV, corresponding to lattice oxygen of CeO 2 and MnO 2 phases (O 2−); denoted as O Ba [27,31]. A broad shoulder at 531.5 eV is ascribed to defective oxides or oxygen species of the surface carbonates and hydroxide (denoted as O a) [14,32]. The ratio of O /O (O a + O Ba) is calculated to be close to 80%, according to the deconvolution of the peak areas by fitting the O 1s pattern, which indicates that the support contains more lattice oxygen species. As we known, O a is the main active oxygen species and is beneficial for the catalytic oxidation of VOCs. Therefore, the support should possess a higher catalytic activity. The valence state of the Pd species in the supporting catalyst is identified further through Pd 3d pattern (Figure 3d). According to Ref. [34], the BEs corresponding to Pd 3d 5/2 with different valences have are slightly different, and the peaks at 337.7–338.4, 336.7–337.2, and 335.0–335.4 eV are attributed to Pd 2+ , Pd 3+ , and Pd 4+ , respectively. In the supporting catalyst, the peak for Pd 3d 5/2 appears at 337.4 eV (i.e. close to 337.2 eV). Therefore, the main valence of the Pd species is determined to be Pd 2+ , in accordance with the XRD result. In addition, the peak at 342.9 eV is attributed to Pd 3d 3/2.

2.2 Redox Properties of the Catalysts

Hydrogen temperature-programmed reduction (H 2 -TPR) measurements were used to investigate the reducibility of catalyst (Figure 4). In the pattern of Ce 0.3 Mn 0.7 , four reduction peaks corresponding to temperatures of 239, 315, 360, and 683 °C were clearly observed. The peaks at 239 and 360 °C are attributed to the reduction of Mn 3+ , with an area ratio of the lower to the higher temperature hydrogen consumption of about 1:2. This is a typical feature of the two-step reduction of MnOx; the low-temperature-reduction peak (239 °C) represents the reduction of MnO 2 to MnO, and the high-temperature-reduction peak (360 °C) refers to the further reduction of MnO to Mn 2 O 3 [35]. The peak at 316 °C may be caused by the synergistic effect between Mn 3+ and Ce 4+ , which would result in the highest activity for VOC oxidation. The peak at 683 °C is assigned to the bulk oxygen species reduction of the CeO 2 phase, according to the TPR pattern of CeO 2 , as shown in Figure S1 of the Supporting Information. In Figure S1, it can be observed that the peak (683 °C) is shifted to a lower temperature compared with that of CeO 2 (746 °C), which may be caused by the interaction between CeO 2 and the MnO 2 phase.

For PdO/Ce 0.3 Mn 0.7 , the reduction peak with the highest intensity was recorded at 87 °C, which may be attributed to the reduction of Pd 2+ species and interaction between the active phase and supports. [36] The peaks at 418 and 694 °C are attributed to the reduction of surface oxygen and bulk oxygen in the CeO 2 phase of the support, respectively. Compared with Ce 0.3 Mn 0.7 , the reduction of the supporting sample starts at a relative low temperature, which indicates that the redox nature of the support is enhanced upon the addition of the active phase and the existence of interactions. In addition, the peak at 240 °C, corresponding to the reduction of Mn 3+ , is also observed; however, the intensity of the peak is weak when comparing with that of Ce 0.3 Mn 0.7 , indicating that the interaction between the active component and the supporter influences the reduction of Mn 3+ .

Oxygen temperature-programmed desorption (O 2 -TPD) is an effective method for determining the mobility of oxygen species. The adsorbed oxygen species on a catalyst changes according to the following procedure: O 2 →O 2 − →O − →O 2− . The physically adsorbed oxygen (O 2 , denoted O Ba ) and chemically adsorbed oxygen (O 2 /O − , denoted O a ) species are much easier to desorb than lattice oxygen (O 2− , denoted O ) species. [39,40] As shown in Figure 5, the mass spectrometry (MS) signal corresponding to the desorption of O 2 is not observed over all catalysts, as O 2 species usually desorb at approximately 50 °C. According to the literature, [23] the peaks between 200 and 500 °C (260/449 °C and 268/460 °C for Ce 0.3 Mn 0.7 and PdO/Ce 0.3 Mn 0.7 , respectively) can be attributed to the chemically adsorbed oxygen species on the vacancies. As we known, the incorporation of metal cations (Mn 3+ ) into CeO 2 could bring about structural deficiencies (O vacancies) into the framework, which can adsorb oxygen molecules from the gas phase under real reaction conditions and be activated to form the active O 2− (i.e. O − or O − ) species, promoting the catalytic efficiency for VOC oxidation. Herein, the oxygen species desorption occurring between 200 and 500 °C could be correlated with the interaction between CeO 2 and MnO 2. Additionally, the desorption peak appearing at higher temperatures (>500 °C) can be at-

![Figure 4. H 2 -TPR results for Ce 0.3 Mn 0.7 and PdO/Ce 0.3 Mn 0.7.](image-url)
tributed to bulk lattice oxygen.\textsuperscript{[40]} For comparison, the O\textsubscript{2}-TPD pattern of CeO\textsubscript{2} is exhibited in Figure S2.

In the O\textsubscript{2}-TPD patterns of the catalysts, it can be seen that the original temperature of O\textsubscript{2} desorption for PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} is higher than that of Ce\textsubscript{0.3}Mn\textsubscript{0.7}, which indicates that a much stronger interaction between PdO and the support exists in PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7}, consistent with the results obtained from XRD and HRTEM.\textsuperscript{[40]} The interaction may be beneficial for VOC oxidation.

2.3 Catalytic Activity of Ce\textsubscript{0.3}Mn\textsubscript{0.7} and PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} for Benzene Oxidation

The catalytic performance of CeO\textsubscript{2}, MnO\textsubscript{x}, Ce\textsubscript{0.3}Mn\textsubscript{0.7}, and PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} catalysts was comparatively evaluated for the oxidation of benzene. The catalytic conversion of benzene as a function of temperature (100–450 °C) is shown in Figure 6a. It can be deemed that PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} achieves complete benzene conversion at about 250 °C, Ce\textsubscript{0.3}Mn\textsubscript{0.7} catalyzes benzene completely at about 400 °C, and the temperature of benzene conversion for CeO\textsubscript{2}/MnO\textsubscript{x} exceeds 500 °C. For a better understanding of the catalytic activity, we highlight the light-off temperatures (T\textsubscript{50} and T\textsubscript{90}) for PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} (204/230 °C) are much lower than those for Ce\textsubscript{0.3}Mn\textsubscript{0.7} (272/369 °C) and pure phase oxide (Table 1). Meanwhile, the reaction rates of the samples at 214 °C (r, mol g\textsubscript{cat}\textsuperscript{-1} s\textsuperscript{-1}) were calculated according to Equation (2), and the data are listed in Table 1 (the benzene conversion is lower than 20%). From the Table 1, it can be acquired that the rate for the PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} sample is 1.46×10\textsuperscript{-4} mol g\textsubscript{cat}\textsuperscript{-1} s\textsuperscript{-1}, which is three times higher than that of CeO\textsubscript{2} (0.49×10\textsuperscript{-4} mol g\textsubscript{cat}\textsuperscript{-1} s\textsuperscript{-1}).

\[
r_{\text{benzene}} = \frac{N_{\text{benzene}} \times X_{\text{benzene}}}{W_{\text{cat}}} \quad (2)
\]

where \(N_{\text{benzene}}\) is the gas flow rate (mol s\textsuperscript{-1}) and \(W_{\text{cat}}\) is the catalyst weight (g).
In addition, the catalytic performance can also be evaluated by comparing the apparent activation energy \( E_a \) values of different catalysts, and the sample with a lower \( E_a \) value will demonstrate superior catalytic activity. The \( E_a \) could be calculated from the slopes of the Arrhenius plots. When the conversion of benzene was below 20\%, benzene oxidation would obey a first-order reaction mechanism with respect to benzene concentration (\( c, \text{ mol g}^{-1} \)). The \( E_a \) values of these samples obtained from the slopes of the linear plots (Figure 6b) are listed in Table 1. It is clearly seen that the \( E_a \) value of PdO/Ce\(_{0.3}\)Mn\(_{0.7}\) (10.91 kJ mol\(^{-1}\)) is lower than those of other catalysts, which further confirms the excellent activity of PdO/Ce\(_{0.3}\)Mn\(_{0.7}\) [Eq. (3)].

\[
E_a = E_f^{\text{V},0} + \frac{1}{2} E_{O_2} - E_1
\]  
(4)

where \( E_f^{\text{V},0} \) and \( E_1 \) are the total energies of the supercell with and without an O vacancy, and \( E_{O_2} \) is the total energy of an \( O_2 \) molecule.

We compare the O vacancy formation energies without and with Mn substitution for Ce. Without Mn, the calculated \( E_1 \) is 3.19 eV. In contrast, the \( E_1 \) decreases to 1.18, 1.84, and 1.98 eV for the cases of \( V_1, V_2, \) and \( V_3 \) with Mn substitution. The distances between Mn and O vacancies (labeled \( V_{1r}, V_{2r}, \) and \( V_{3r} \)) are calculated to be 2.03, 4.36, and 5.92 Å, respectively. These results mean that the Mn substitution significantly lowers the energy cost of O vacancy formation, and the lowering effect becomes weaker as the vacancy distance increases. This is easily understood, because the radius of a Mn atom is smaller than that of a Ce atom, and thus allows further relaxation of the atoms around the vacancy, which would compensate a higher energy loss through the missing of Ce–O bonds. In other words, the O vacancy is easier to form because of the replacement of Mn for Ce atoms. Given the central role of an O vacancy in a catalyst, \( E_1 \) is expected to give a better performance than the pure phase, which is consistent with the benzene catalytic degradation results.

To further research the status of oxygen vacancies and benzene adsorption during the whole catalytic process in order to understand the corresponding mechanism, in situ Raman and...
FTIR spectroscopy were measured. Figure 8 exhibits the in situ Raman spectra of CeO$_2$ and Ce$_{0.7}$Mn$_{0.3}$O$_2$. Through the pattern of pure CeO$_2$ (Figure 8a), it can be observed that four bands exist at 250, 456, 597, and 1050 \text{ cm}^{-1}, in which the peak at 456 \text{ cm}^{-1} is attributed to a $F_{2g}$ Raman band from the space group $Fm\overline{3}m$ of a cubic fluorite structure.\[^{[50]}\] This peak is very sensitive to the disorder degree of surface lattice oxygen. The two peaks at 250 and 1050 \text{ cm}^{-1} are assigned to second-order transverse and longitudinal vibration modes of the cubic CeO$_2$ fluorite phase.\[^{[51]}\] The peak at 597 \text{ cm}^{-1} is indicative of the presence of defect-induced (D) modes.\[^{[52–54]}\] It can also be seen that the shape and intensity of the main peak (456 \text{ cm}^{-1}) experience little change; however, the width broadens gradually when the temperature increases, which may be related with the size of the CeO$_2$ particles.\[^{[55]}\]

For Ce$_{0.7}$Mn$_{0.3}$O$_2$ (Figure 8b), there are four peaks in the pattern that exist at 258, 350, 442, and 636 \text{ cm}^{-1}; a shoulder at 575 \text{ cm}^{-1} can be also observed. The bands at 258 and 442 \text{ cm}^{-1} are attributed to the characteristic peaks of CeO$_2$ described above, whereas the bands at 350 and 636 \text{ cm}^{-1} correspond to the surface bending vibration of MnO$_2$ and symmetric stretching vibration of Mn–O, respectively.\[^{[56, 57]}\] The shoulder at 575 \text{ cm}^{-1} is ascribed to oxygen vacancies. In is worthy noting that the position of the main peak, corresponding to the $F_{2g}$ vibration, is shifted from 456 to 442 \text{ cm}^{-1}, as compared with that of CeO$_2$ (Figure 8a); this can be attributed to the formation of surface oxygen vacancies.\[^{[58]}\] Meanwhile, the intensity and symmetry of the main peak become worse with increasing temperature, which is also caused by crystal structural defects.\[^{[58]}\] The removal of surface active oxygen results in the formation of oxygen vacancies. The ratio of the integrated peak area for oxygen vacancies (ca. 575 \text{ cm}^{-1}) to that of the main peak (442 \text{ cm}^{-1}), defined as $A_{\text{sp}}/A_{\text{tot}}$, is used here to characterize the relative amount of oxygen vacancies. It can be observed that the ratio of $A_{\text{sp}}/A_{\text{tot}}$ increases to about 0.276 at 360 °C from 0.119 at room temperature (RT). Surface oxygen can be considered to adsorb favorably on an oxygen vacancy.\[^{[59]}\] The result verifies the involvement of surface oxygen in benzene oxidation.

In situ FTIR spectra of Ce$_{0.7}$Mn$_{0.3}$ and PdO/Ce$_{0.7}$Mn$_{0.3}$ collected at different temperatures are shown in Figure 9. In the pattern of the Ce$_{0.7}$Mn$_{0.3}$ composite at 100 °C (Figure 9a), the bands at 1569 and 1502 \text{ cm}^{-1} can be assigned to the C=C degenerate stretching vibrations of the aromatic ring.\[^{[60]}\] The band at 1596 \text{ cm}^{-1} is related to the formation of a π-complex between surface metal ions (acceptor, Lewis acid site) and the aromatic ring (donor, Lewis base site).\[^{[61]}\] As we know, the metal ions possess empty electronic orbits, which can be filled with π-electron; therefore, the benzene molecule can be absorbed at the surface of the catalyst. It is interesting to note that the band at 1636 \text{ cm}^{-1} is predominant, accompanied by the appearance of a band at 1308 \text{ cm}^{-1}. The two bands are attributed to a surface enolic species;\[^{[62, 63]}\] however, the intensity becomes weak and even disappears with increasing temperature, indicating that enolic species are partially oxidized surface species. The pattern of the catalyst at 400 °C is exhibited separately (inset picture), owing to the relatively weak peak intensity in the original image, and this is beneficial to identify the bands in detail. The resulting spectrum exhibits bands at 1357 and 1548 \text{ cm}^{-1}, which are assigned to carbonate bidentate, whereas bands at 1413 and 1522 \text{ cm}^{-1} are ascribed to the asymmetric stretching vibration of acetate-type carboxylates.\[^{[59, 64–67]}\] In addition, the peak at 1223 \text{ cm}^{-1} may corresponded to the

![Figure 8](image1.png)

**Figure 8.** In situ Raman spectra of CeO$_2$ (a) and Ce$_{0.7}$Mn$_{0.3}$ (b).

![Figure 9](image2.png)

**Figure 9.** In situ FTIR spectra of Ce$_{0.7}$Mn$_{0.3}$ (a) and PdO/Ce$_{0.7}$Mn$_{0.3}$ (b).

\[59\]
\[60\]
\[61\]
\[62\]
\[63\]
\[59, 64–67\]
the bands corresponding to the stretching vibration of C–C bonds in aliphatic species,\textsuperscript{68} which are formed through the breakage of the benzene ring.

For PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7}, the in situ FTIR band at 100 °C (Figure 9b) is similar to that of Ce\textsubscript{0.3}Mn\textsubscript{0.7}. The difference is that the band at 1223 cm\textsuperscript{-1} is more clearly discerned compared with that of Ce\textsubscript{0.3}Mn\textsubscript{0.7}, which indicates that the absorbed benzene molecule may be more easily oxidized, with the surface active oxygen species breaking the ring at lower temperatures. The intensities of all of the bands also become weaker as the temperature increases; therefore, the spectrum of the catalyst at 400 °C is shown separately to identify each peak as described above (in inset picture of Figure 9b). The bands at 1362 and 1558 cm\textsuperscript{-1} are attributed to carbonate bidentate species and the bands at 1412 and 1523 cm\textsuperscript{-1} correspond to stretching vibration of carboxylates. The peaks at 1455, 1473, and 1488 cm\textsuperscript{-1} belong to stretching vibrations of the aromatic ring and the bands at 1335 and 1318 cm\textsuperscript{-1} are assigned to C–H vibrations of benzene.\textsuperscript{69} The bands corresponding to the stretching vibration of C–C can be also distinguished at 1225 cm\textsuperscript{-1}.

Based on the analysis above, it can be seen that the process of benzene oxidation contains several elementary steps (Figure 10): 1) the formation of a π-complex of benzene adsorption during the interaction of the benzene ring with the catalyst; 2) a gas-phase oxygen molecule is activated at the surface of the catalyst to adsorb at surface vacancies; 3) the attack of active surface oxygen species (O\textsubscript{2−} or O\textsuperscript{−}) occurs and lattice oxygen is released from the catalyst to the benzene ring; 4) partially oxidized surface products are formed, including enolic and acetate-type carboxylate species; 5) further oxidation occurs to form the reaction products (CO\textsubscript{2} and H\textsubscript{2}O). It is worth noting that the activation of gas-phase oxygen and benzene-ring breakage are key steps, during which more oxygen vacancies are formed or replenished, owing to the release of lattice oxygen and the formation of surface active oxygen species. Therefore, the role of oxygen vacancies in storing and transporting the active oxygen cannot be ignored. For PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7}, the interaction between the active phase and the supporter can influence the surface energy, so that lattice oxygen can be released more easily to produce more oxygen vacancies. Therefore, PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} possesses a higher catalytic activity.

3. Conclusions

A Ce\textsubscript{0.3}Mn\textsubscript{0.7} composite oxide synthesized through a hydrothermal method was chosen as the supporter to load PdO. The catalytic activities of Ce\textsubscript{0.3}Mn\textsubscript{0.7} and PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} for benzene oxidation were researched and compared with those of pure oxides. The results indicate that Ce\textsubscript{0.3}Mn\textsubscript{0.7} and PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} possess higher activities, and the latter is the best candidate. For Ce\textsubscript{0.3}Mn\textsubscript{0.7}, more oxygen vacancies are formed, as Ce\textsuperscript{4+} is replaced by Mn ions, and this is responsible for the higher activity. DFT was adopted to calculate the formation energy of oxygen vacancies and the data also identify that Ce\textsubscript{0.3}Mn\textsubscript{0.7} can form oxygen vacancies more easily than pure CeO\textsubscript{2}. For PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7}, the interaction between the active phase and the supporter determines the catalytic properties other than oxygen vacancies. In situ Raman and FTIR spectra were used to analyze the oxygen vacancies, the involvement of oxygen species, and the formation of intermediates during the whole catalytic process, so as to research the mechanism. The results demonstrate that benzene oxidation proceeds through several steps and oxygen vacancies play an important part.

**Experimental Section**

**Preparation of CeO\textsubscript{2}–MnO\textsubscript{2} and PdO/CeO\textsubscript{2}–MnO\textsubscript{2}**

The chemicals used in this work, including Ce(NO\textsubscript{3})\textsubscript{3}•6H\textsubscript{2}O (99%), Mn(NO\textsubscript{3})\textsubscript{2} solution (50%), NaOH (98%), sodium citrate (Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}•2H\textsubscript{2}O, 99%), sodium tetrachloropalladate (Na\textsubscript{2}PdCl\textsubscript{4}), and ethanol were purchased from Beijing Chemicals Company (Beijing, China). The CeO\textsubscript{2}–MnO\textsubscript{2} composite oxide (atomic ratio of Ce/Mn is 3:7) was synthesized by using a hydrothermal process according to our previously reported experimental operations and labeled as Ce\textsubscript{0.3}Mn\textsubscript{0.7}.\textsuperscript{[10]} Pure CeO\textsubscript{2} and MnO\textsubscript{2} were also prepared by using a similar process as a reference. PdO/Ce\textsubscript{0.3}Mn\textsubscript{0.7} was synthesized through reduction deposition.\textsuperscript{[58]} Firstly, Ce\textsubscript{0.3}Mn\textsubscript{0.7} (as the support) was mixed with Na\textsubscript{2}PdCl\textsubscript{4} solution (0.01 M, 10 mL), and then Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}•2H\textsubscript{2}O was added into the solution. After the reaction, the precipitates were collected and washed. Finally, the precursors were dried under vacuum at 80 °C overnight, followed by calcination in air at 400 °C for 2 h.

**Characterization**

The crystal phase of the materials was characterized by using XRD (Philips Xpert PRO) with a CuK\textsubscript{α} radiation source (λ = 0.154187 nm) at a scanning rate of 0.03° s\textsuperscript{-1} (2θ from 10 to 90°). ICP measurements were performed to identify the contents of Ce and Mn elements in the support and Pd in the loading catalyst. The morphologies and structures of the samples were observed by using TEM (Tecnai G2 F20 U-TWIN) with an accelerating voltage of 200 kV. Aberration-corrected annular bright-field scanning transmission electron microscopy was performed by using a JEOL JARM200F TEM equipped with two CEOS probe aberration correctors. The surface compositions were determined through XPS by using an ESCALab220i-XL electron spectrometer from VG Scientific with a monochromatic AlK\textsubscript{α} radiation. The BE was referenced to the C 1s line at 284.8 eV from adventitious carbon.

H\textsubscript{2}-TPR was performed with a U-type quartz reactor equipped with an automated catalyst characterization system (Autochem 2920,
Micromeritics). A 50 mg sample (40–60 mesh) was loaded and pretreated with a 5 % O₂ and 95 % He mixture (30 mL min⁻¹) and kept at 150 °C for 1 h before cooling to 50 °C under a He flow. The samples were then heated to 900 °C at a rate of 10 °C min⁻¹ under the flow of a 10 % H₂ and 90 % Ar mixture (50 mL min⁻¹). O₂-TPD was carried out in a U-shaped quartz tube and the desorption signal of oxygen was recorded with on-line mass spectrometer apparatus (HIDEN QIC-20). Prior to O₂-TPD testing, the sample (50 mg) was pretreated in a purified oxygen stream (50 mL min⁻¹) at 400 °C for 60 min, cooled to room temperature in an oxygen atmosphere, and purged with a stream of purified He until stabilization of the MS base line was achieved. The reactor was heated at a rate of 10 °C min⁻¹ from 50 to 700 °C. Simultaneously, the desorbed oxygen signal was collected with the MS detector.

In situ Raman spectra were obtained on a spectrometer equipped with a CCD detector (Horiba Jobin Yvon HR800). The catalyst samples were excited with a 514.5 nm Ar ion laser in an in situ reactor, which is capable of selecting heating samples from RT to 600 °C under flowing gases. The laser power was 10 mW and the scanning time was 60 s, with resolution of 1–1.3 cm⁻¹. All samples were pretreated for 1 h in the flow of Ar (50 mL min⁻¹, 0.1 MPa) at 250 °C before Raman spectra were collected at RT. For benzene oxidation, the pretreated samples (50 mg) were exposed to the reaction gas (500 ppm benzene and 20 % O₂/N₂, 50 mL min⁻¹). Then, the sample was heated at a rate of 10 °C min⁻¹ from 30 to 350 °C. Every temperature point was held for 1 h to record the Raman spectra.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted on a Nicolet 6700 FTIR fitted with a liquid-nitrogen-cooled mercury-cadmium–telluride detector (MCT). The DRIFTS cell (Harrick, HVC-DRP) fitted with CaF₂ windows was used as the reaction chamber, which allowed samples to be heated to 600 °C. All spectra were within the range of 4000–1200 cm⁻¹, at a resolution of 4 cm⁻¹, and 64 scans were collected. Prior to benzene adsorption and oxidation experiments, the samples were pretreated with N₂ at 400 °C for 2 h and with 10 % O₂/N₂ at 400 °C for 2 h. Then, the samples were cooled to 100 °C to remove the contaminants. The spectra of the samples (50 mg) were recorded from 100 to 350 °C under different conditions. For CB oxidation, the composition of the feed stream was same as that for the catalytic performance test.

**Catalytic Activity Tests**

Activity tests for the catalytic oxidation of benzene over Ce₀.₃Mn₀.₇, and PdO/Ce₀.₃Mn₀.₇ catalysts were performed in a continuous-flow fixed-bed reactor under atmospheric pressure; the reactor contained 100 mg of each catalyst sample (40–60 mesh). To facilitate the horizontal comparison of the subsequent results, the composition of the testing gases required that a pure airflow (50 mL min⁻¹) was mixed with another airflow containing gaseous benzene (1000 ppm, 50 mL min⁻¹) with a total flow rate of 100 mL min⁻¹. The weight hourly space velocity (WHSV) was typically 60000 mL g⁻¹ h⁻¹. The products were analyzed on-line by using GC–MS (Hewlett-Packard 6890N gas chromatograph interfaced to a Hewlett-Packard 5973N mass-selective detector) with a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm).

To assess the effect of water vapor on the catalytic activities of Ce₀.₃Mn₀.₇ and PdO/Ce₀.₃Mn₀.₇, the on-stream benzene oxidation experiments were carried out in the presence and absence of 1.5 vol% water vapor. Typically, an airflow (50 mL min⁻¹) was used for bubbling water before it was mixed with another airflow containing gaseous benzene (50 mL min⁻¹). The mixed gas containing water vapor (1.5 vol%) and benzene (500 ppm) was used for catalytic tests and the WHSV of the mixed gas was still 60000 mL g⁻¹ h⁻¹.

**Reaction Kinetics Tests**

The kinetics parameters were measured in the fixed-bed reactor for benzene oxidation, as mentioned above, and the catalytic reaction data were obtained after the reaction was stable for 60 min with a complete conversion of benzene lower than 20 % at different temperatures.

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