Simultaneous catalytic oxidation of elemental mercury and arsine over $\text{CeO}_2(111)$ surface: A density functional theory study

Yingjie Zhang

Dali University

Huijuan Yu

Dali University

Xueqian Wang (✉ xqwang214@163.com)

Kunming University of Science and Technology <https://orcid.org/0000-0001-9202-2191>

Langlang Wang

Kunming University of Science and Technology

Yuancheng Li

Dali University

Dongpeng Lv

Dali University

Dan Zhu

Dali University

Chunmei Tian

Dali University

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Abstract

Ceria (CeO_2) based materials are potential catalysts for the removal of the Hg^0 and AsH_3 present in reducing atmospheres. However, theoretical studies investigating the Hg^0 and AsH_3 removal capacity of ceria remain limited. In this study, the adsorption behavior and mechanistic pathways for the catalytic oxidation of Hg^0 and AsH_3 on the $\text{CeO}_2(111)$ surface, including the calculation of optimized adsorption configurations and energies, were investigated using density functional theory calculations. The results suggest that Hg^0 and AsH_3 are favorably adsorbed on the $\text{CeO}_2(111)$ surface, whereas CO is not, which is crucial for selective removal when CO is a desirable gas component. Further, AsH_3 is adsorbed more favorably than Hg^0 . In addition, the calculations revealed that the Hg atom is initially adsorbed on the surface and then oxidized by lattice oxygen to form HgO. Concerning AsH_3 decomposition, the stepwise dehydrogenation of AsH_3 followed by bonding with lattice O atoms to form As-O bond seems the most plausible. Finally, the adsorbed As-O bond is further formed elemental As and As_2O_3 . Therefore, CeO_2 can adsorb and remove Hg^0 and AsH_3 , making it a promising catalyst for the simultaneous catalytic oxidation of Hg^0 and AsH_3 in strongly reducing off-gas.

1. Introduction

Yellow phosphorus is an important raw material. The production of each ton of yellow phosphorus produces about 2500–3000 m^3 of off-gas, and the CO content of this gas is high (80–95%), making it an important C1 chemical raw material. However, in addition, to CO, pollutants, including H_2S , elemental mercury (Hg^0), and arsine (AsH_3), are present in the phosphorus off-gas [1]. Atmospheric heavy metal pollution seriously threatens human health and environmental safety, and the phosphorus industry is a major contributor to this, especially in southwest China. Therefore, laws and regulations have been developed to prevent and control pollution [2]. To comply with these increasingly stringent requirements, several purification and resource utilization technologies have been developed to treat yellow phosphorus off-gas, and the removal of Hg^0 and AsH_3 has received particular attention because of their high toxicity, volatility, and persistence in the environment [3, 4]. In addition to the health risks, the presence of Hg^0 and AsH_3 in yellow phosphorus off-gas limits its use as a raw material in other processes [5]. Therefore, Hg^0 and AsH_3 removal technology is urgently needed.

Mercury in the gas phase mainly exists in three forms: particulate-bound mercury (Hg^{p}), elemental mercury (Hg^0), and oxidized mercury (Hg^{2+}) [6]. Hg^{2+} is easily soluble in water, and Hg^{p} remains in the atmosphere for an extremely short time. Therefore, both of these species can be captured by electrostatic precipitators, fabric filters, and wet scrubbers [7–9]. However, Hg^0 is difficult to dissolve in water or adsorb on solid surfaces because of its high vapor pressure and low water solubility [10]. In contrast, arsenic can be dispersed in the gas phase as oxidized (As_2O_5 , As_2O_3 , and arsenate) and reduced (AsH_3) species [5]. In

yellow phosphorus off-gas, which is a highly reducing mixture, mercury mainly exists as Hg^0 , whereas arsenic mainly exists as AsH_3 [11]. Therefore, Hg^0 and AsH_3 removal has become a research focus.

Currently, the main methods of Hg^0 and AsH_3 removal involve adsorption and catalytic oxidation [12]. In particular, noble metal catalysts, such as Au [13], Ag [14], Pd [15, 16], Pt [17], Ru [18], and Ir [19], have excellent catalytic activity. These materials have, thus, been used as adsorbents and catalysts to remove Hg^0 and AsH_3 . However, the high cost of noble metals has limited their commercialization and application. Fortunately, noble-metal-modified carbon materials, which are significantly cheaper than pure noble metals, also show catalytic effects [19, 20]. In addition, single or binary metal oxides, especially transition metal oxides, other modified carbon materials, zeolites, and molecular sieves have been reported to show high Hg^0 and AsH_3 removal efficiencies [21–24]. However, because of the high reactivity of CO, most catalysts will also react with this useful molecule. Further, the use of separate equipment or catalysts to remove Hg^0 and AsH_3 would result in significant capital investment for equipment and increase operating costs and process complexity. Therefore, selective catalysts for Hg^0 and AsH_3 removal from reducing gas mixtures are required.

Key to developing selective catalysts for Hg^0 and AsH_3 removal is finding a material that lowers the energy barriers of the oxidizing reactions. Ceria is a promising catalytic oxidation material with low cost, no toxicity, and a large oxygen storage capacity. Crucially, CeO_2 contains the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple, which can vary from CeO_2 to Ce_2O_3 and vice versa under oxidizing and reducing atmospheres, respectively [25, 26]. To date, there have been many studies on the application of ceria catalysts. Li et al. and Fan et al. showed that CeO_2 has superior catalytic performance for the oxidation of Hg^0 , having 90% oxidation efficiency in simulated flue gas [25, 27]. Xie et al. [28] also used ceria to achieve a high AsH_3 removal efficiency. Zhao et al. reported the modification of a commercial selective catalytic oxidation (SCR) catalyst with a series of metal oxides and found that CeO_2 -modified SCR catalyst showed the highest Hg^0 oxidation capacity [29]. In addition, in our previous work, we found that CeO_2 can oxidize Hg^0 and AsH_3 in a reducing atmosphere [5, 28]. Specifically, the removal efficiency was better than 90% at a low reaction temperature of 150 °C. X-ray photoelectron spectroscopy (XPS) measurements showed that Hg^0 and AsH_3 are converted to HgO , elemental As, and As_2O_3 on the catalyst surface, suggesting that Hg^0 and AsH_3 are oxidized to these species by the lattice oxygen on the surface of the catalyst, and the mechanism of heterogeneous Hg^0 and AsH_3 oxidation should follow the Mars–Maessen mechanism [5].

Nevertheless, few theoretical investigations of the mechanism of Hg^0 and AsH_3 oxidation over ceria have been carried out, and, to date, there have been no reports of quantum chemistry studies concerning the reaction pathway over the $\text{CeO}_2(111)$ surface. In this study, based on our previous work, we systematically and comprehensively studied the adsorption of Hg, CO, and AsH_3 on the $\text{CeO}_2(111)$ surface using density functional theory (DFT) to assess the feasibility of the simultaneous catalytic oxidation of Hg^0 and AsH_3 over CeO_2 for the treatment of yellow phosphorus off-gas. As a result, the

reaction pathways and energy barriers were studied and assessed. The objective of this work is to provide theoretical guidance for the development of catalysts for the simultaneous oxidation of Hg^0 and AsH_3 in reducing gas mixtures.

2. Materials And Methods

2.1. Computational methods

All calculations in this work were carried out by the Dmol3 program included in the Materials Studio based on density function theory (DFT) [30, 31]. The exchange-correction potential was modeled using the generalized gradient approximation (GGA) type Perdew–Burke–Ernzerhof (PBE) functional [32, 33]. The inner and outer electrons were described by the projector augmented wave (PAW) function [34]. The energy of the system was minimized without any symmetry constraints.

A 10 Å thick vacuum layer was used to prevent mirror interactions between ceria layers in the supercell, and a cutoff energy of 450 eV was used throughout the calculations. Further, a $3 \times 3 \times 1$ Monkhorst Pack k-point grid was used during geometry optimization. The width for Gaussian smearing was 0.2 eV, and the geometric convergence criteria for the energy change tolerance and maximum force tolerance were 10^{-5} eV/atom and 0.05 eV/Å, respectively. These values were chosen to enable accurate but practical calculations because of the complex surface structure. Transition states were confirmed by the presence of a single imaginary frequency.

The adsorption energy (E_{ads}) describes the adsorption strength between catalyst surface and corresponding gases, as given by Eq. (1) [35, 36].

$$E_{\text{ads}} = E_{\text{total}} - (E_1 + E_2) \quad (1)$$

Here, E_{total} , E_1 , and E_2 represent the adsorption energies of the whole adsorption system on the $\text{CeO}_2(111)$ surface, pure catalyst, and isolated free molecules, respectively. If the value of E_{ads} is negative, the adsorption process is favorable, and when the absolute value of E_{ads} exceeds 0.5 eV, the adsorption process results in stable chemical adsorption [37].

2.2. Atomic model of $\text{CeO}_2(111)$ surface

CeO_2 has a cubic fluorite crystal structure [38] containing four Ce^{4+} ions and eight O^{2-} ions in the unit cell. Usually, adsorption occurs at the crystal surface rather than in the crystal bulk, so we studied the adsorption behavior on one crystal surface, which is not only more practical, but also reduced the workload. There are three low index surfaces of crystalline CeO_2 : (111), (110), and (100) [39]. The most stable surface in CeO_2 is the (111) surface, which is formed of a continuous O-Ce-O network interlayer structure. Therefore, this surface was selected as a representative model to study. The CeO_2 supercell structure is shown in Figs. 1(a) and 1(b), and the constructed $\text{CeO}_2(111)$ surface model is shown in Fig.

1(c) and 1(d). The optimized CeO₂ supercell parameters were consistent with those from the literature ($a = 10.98 \text{ \AA}$, $b = 10.98 \text{ \AA}$, $c = 16.78 \text{ \AA}$).

There are four active sites on CeO₂(111) surface: O top, Ce top, O-O bridge, and Ce-O bridge, as shown in Fig. 2. A $2 \times 2 \times 1$ supercell structure was used to study the adsorption of Hg⁰, AsH₃ and CO on the CeO₂(111) surface. As mentioned in Section 2, a 10 Å thick vacuum region was used to eliminate unphysical interactions between adjacent slabs [40].

3. Results And Discussions

3.1. Hg⁰, AsH₃, and CO adsorption on the CeO₂(111) surface

Homogeneous oxidation efficiency is typically low (nearly zero), so we studied the interactions between gases and catalyst surface [41]. Adsorption is the first step in the catalytic reaction over a solid catalyst, therefore, we studied the interactions between the key atoms and molecules (Hg⁰, AsH₃, and CO) and the CeO₂(111) surface. The adsorption analysis revealed important information that guided our subsequent search for the key structures on the reaction pathway.

First, the adsorption of Hg⁰ on the O top, Ce top, O-O bridge, and Ce-O bridge sites was investigated, as shown in Fig. 3. The corresponding adsorption energies and structural parameters are listed in Table 1. The adsorption energies for Hg⁰ on the Ce top, Ce-O bridge, O top, and O-O bridge sites decreased in that order: -0.121, - 0.078, - 0.043, and - 0.027 eV, respectively, indicating that the Ce top site is the most stable site for Hg⁰ adsorption. The separation between Hg and Ce in this adsorption mode is 3.241 Å.

Table 1
Adsorption energies and structural parameters for Hg⁰
adsorbed on the CeO₂(111) surface.

Adsorption site	$E_{\text{ads}} / \text{eV}$	$d_{\text{Hg-Ce}} / \text{\AA}$	$d_{\text{Hg-O}} / \text{\AA}$
Ce top	-0.121	3.241	-
Ce-O bridge	-0.078	3.478	3.216
O top	-0.043	-	3.367
O-O bridge	-0.027	3.691	3.427

Next, we studied the adsorption of AsH₃ on the CeO₂(111) surface to understand the competitive adsorption of Hg⁰ and AsH₃. The adsorption configurations of AsH₃ on the O top, Ce top, O-O bridge, and Ce-O bridge sites were investigated, and the adsorption energies for these sites were found to be - 1.213, - 1.391, - 1.271, and - 1.313 eV, respectively. The optimized configurations for AsH₃ adsorption on

CeO₂(111) surface are shown in Fig. 4, and the corresponding adsorption energies and structural parameters are listed in Table 2. The adsorption AsH₃ is energetically more favorable than that of Hg⁰, and the most stable binding site for AsH₃ adsorption was the Ce top site. In this configuration, the separation between As and the Ce atom is 2.772 Å.

Table 2
Adsorption energies and structural parameters for AsH₃ adsorbed on the CeO₂(111) surface.

Adsorption site	<i>E</i> _{ads} / eV	<i>d</i> _{AsH3-Ce} / Å	<i>d</i> _{AsH3-O} / Å
Ce top	-1.391	2.772	-
Ce-O bridge	-1.313	2.928	2.895
O top	-1.213	-	2.697
O-O bridge	-1.271	2.881	2.718

Finally, the adsorption of CO on the CeO₂(111) surface was studied (Fig. 5), and the adsorption energies and structural parameters are listed in Table 3. The adsorption energies for CO on the O top, Ce top, O-O bridge, and Ce-O bridge sites are 0.034, 0.097, 0.101, and 0.142 eV, respectively. Importantly, all these values are positive, indicating that CO adsorption on the CeO₂(111) surface is unfavorable.

Table 3
Adsorption energies and structural parameters for CO adsorbed on the CeO₂(111) surface

Adsorption site	<i>E</i> _{ads} / eV	<i>d</i> _{CO-Ce} / Å	<i>d</i> _{CO-O} / Å
Ce top	0.097	3.472	-
Ce-O bridge	0.142	3.428	3.495
O top	0.034	-	3.497
O-O bridge	0.101	3.488	3.518

Therefore, in terms of the adsorption energies, on the CeO₂(111) surface, AsH₃ adsorption is most favorable, followed by Hg⁰ adsorption; in contrast, CO adsorption is unfavorable. These results are consistent with our experimental observations that CeO₂ can adsorb and remove Hg⁰ and AsH₃ in a strongly reducing atmosphere [5].

3.2. Mechanism of Hg⁰ catalytic oxidation over the CeO₂(111) surface

In our previous experimental study, we found that HgO is formed on the catalyst surface, suggesting that lattice oxygen in the catalyst plays an important role in the heterogeneous oxidation process, crucially, the consumed lattice oxygen is replenished by gas phase oxygen [5]. Therefore, we next discuss the possible

Hg^0 catalytic oxidation reaction based on the Mars-Maessen mechanism. The proposed reaction pathway is shown in Fig. 6 for the following steps: reactant $\rightarrow$ intermediate 1 (IM1) $\rightarrow$ transition state 1 (TS1) $\rightarrow$ product. All energy barriers are relative to the reactant. The optimized geometries of the intermediates, transition states, and products in reaction pathway are shown in Fig. 7. In this model, Hg is initially adsorbed on the surface and then oxidized by the lattice oxygen to form HgO. The TS1 transition state had a single imaginary frequency of -72.45 cm^{-1} , and the energy barrier to form HgO was calculated to be 0.21 eV.

3.3. Mechanism of AsH_3 catalytic oxidation over the $\text{CeO}_2(111)$ surface

Based on our previous studies [5, 28], AsH_3 is absorbed on the ceria surface, decomposed, and then, oxidized by lattice oxygen to form elemental As and As_2O_3 . Furthermore, there are two possible pathways for AsH_3 decomposition on the $\text{CeO}_2(111)$ surface. The combination of AsH_3 with O atoms of $\text{CeO}_2(111)$ surface followed by dehydrogenation or gradual dehydrogenation and the formation of bonds with O atoms from the $\text{CeO}_2(111)$ surface. Two possible AsH_3 molecule decomposition pathways are proposed: pathway I (reactant $\rightarrow$ IM2 $\rightarrow$ TS2 $\rightarrow$ IM3 $\rightarrow$ TS3 $\rightarrow$ IM4 $\rightarrow$ TS4 $\rightarrow$ IM5 $\rightarrow$ IM6) and pathway II (reactant $\rightarrow$ IM2 $\rightarrow$ TS5 $\rightarrow$ IM7 $\rightarrow$ TS6 $\rightarrow$ IM8 $\rightarrow$ TS7 $\rightarrow$ IM9 $\rightarrow$ IM10), as shown in Fig. 8 with relative energy barriers.

In the case of pathway I, the optimized geometries of the intermediates and transitions states for AsH_3 decomposition on the $\text{CeO}_2(111)$ surface are shown in Fig. 9. In this pathway, AsH_3 is initially adsorbed on the surface and then combined with lattice oxygen at the surface. Then, the AsOH_3 intermediate is formed (IM2 $\rightarrow$ TS2 $\rightarrow$ IM3; imaginary frequency: -65.45 cm^{-1}), which has an energy barrier of 1.23 eV. Next, the first As-H bond is broken to form the $\text{AsOH}_2 + \text{H}$ intermediate (IM3 $\rightarrow$ TS3 $\rightarrow$ IM4; imaginary frequency: -84.34 cm^{-1}), which has an energy barrier of 0.72 eV. Subsequently, the second As-H bond is broken to form the $\text{AsOH} + 2\text{H}$ intermediate (IM4 $\rightarrow$ TS4 $\rightarrow$ IM5; imaginary frequency: -102.45 cm^{-1}), which has an energy barrier of 0.47 eV. Finally, the third As-H bond is broken in a spontaneous process (IM5 $\rightarrow$ IM6) to yield As-O bond bound to the surface, as well as three H atoms. Thus, one AsH_3 molecule is decomposed by stepwise breakage to one As-O bond on the $\text{CeO}_2(111)$ surface.

Figure 10 presents the optimized geometries of the intermediates and transition states for AsH_3 decomposition on $\text{CeO}_2(111)$ surface via pathway II. First, AsH_3 is adsorbed on the surface, and then, the first As-H bond is broken to yield an $\text{AsH}_2 + \text{H}$ intermediate (IM2 $\rightarrow$ TS5 $\rightarrow$ IM7; imaginary frequency: -34.67 cm^{-1}), which has an energy barrier of 0.72 eV. Next, the second As-H bond is broken to form the $\text{AsH} + 2\text{H}$ intermediate (IM7 $\rightarrow$ TS6 $\rightarrow$ IM8; imaginary frequency: -79.34 cm^{-1}), which has an energy barrier of 0.93 eV. And then, As + 3H is formed as the third As-H bond is broken (IM8 $\rightarrow$ TS7 $\rightarrow$ IM9; imaginary frequency: -47.92 cm^{-1}). This step has an energy barrier of 0.30 eV. Finally, the adsorbed As forms a bond with surface O spontaneously (IM9 $\rightarrow$ IM10) in a barrierless process, yielding an As-O bond

and three H atoms. Comparing the two possible reaction pathways, pathway II has the lowest energy barrier. Hence, the stepwise dehydrogenation of AsH₃ followed by the formation of a bond with an O atom of the CeO₂(111) surface seems the most plausible mechanism.

The length of the As-O bond in the As-O bond formed from AsH₃ is 1.86 Å, which is similar to that in As₂O₃, which may be the final product. Therefore, to determine the final products of the catalytic oxidation of AsH₃, we carried out calculations on three As-O bonds on the CeO₂(111) surface. This resulted in the formation of elemental As and As₂O₃. The proposed reaction pathway (IM10 → TS8 → IM11 → TS9 → IM12 → product) is shown in Fig. 11 with relative energy barriers. First, two As-O bonds overcome energy barrier to generate a new As-O bond, to form As-O + As-O-As-O intermediate (IM10 → TS8 → IM11; imaginary frequency: -74.24 cm⁻¹), this process has an energy barrier of 0.18 eV. Next, a new As-O bond is formed to yield an As-O-As-O-As-O intermediate (IM11 → TS9 → IM12; imaginary frequency: -93.23 cm⁻¹) in a process having an energy barrier of 0.67 eV. Finally, a further As-O bond is broken spontaneously, and IM12 is converted to the products: elemental As and As₂O₃. The optimized geometries are shown in Fig. 12. The calculation results are consistent with our experimental observations [5]. Thus, overall, AsH₃ is dehydrogenated stepwise and then forms bonds with O on the CeO₂(111) surface to yield elemental As and As₂O₃.

4. Conclusions

In this work, we systematically studied the adsorption and catalytic oxidation of Hg⁰ and AsH₃ on the CeO₂(111) surface. Comparing the adsorption energies and the adsorption configurations of Hg⁰, AsH₃, and CO, we found that the most stable binding sites for Hg⁰ and AsH₃ are the Ce-top sites, having adsorption energies of -0.121 and -1.391 eV, respectively. In addition, the adsorption energy for CO was positive. Thus, AsH₃ adsorption is most favorable, followed by that of Hg⁰, whereas CO adsorption on CeO₂(111) is unfavorable. This result suggests that CeO₂ could selectively adsorb and remove Hg⁰ and AsH₃ in strongly reducing gas mixtures, such as yellow phosphorous off-gas. In addition, the reaction mechanisms were investigated using DFT calculations. The catalytic oxidation of Hg⁰ follows the Mars-Maessen mechanism: Hg atoms are first adsorbed on the surface and then oxidized by the lattice oxygen to form HgO. In contrast, AsH₃ is gradually dehydrogenated and forms bonds with an O atom of CeO₂(111) surface to yield As-O bond. Finally, the As-O bonds are converted to elemental As and As₂O₃. The results of this study provide an understanding of Hg⁰ and AsH₃ adsorption and catalytic oxidation on the CeO₂ surface, and we conclude that ceria is a promising catalyst for the removal Hg⁰ and AsH₃ from strongly reducing off-gases.

Declarations

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Competing interest

The authors have no relevant financial or non-financial interests to disclose.

Author contributions

All authors contributed to the study conception and design. Methodology, Writing- Original draft preparation, Investigation were performed by Yingjie Zhang, Writing- Reviewing and Editing; Conceptualization were performed by Huijuan Yu, Funding acquisition were performed by Xueqian Wang, Writing- Reviewing and Editing were performed by Langlang Wang and Chunmei Tian, Investigation, Funding acquisition were performed by Yuancheng Li, Data curation were performed by Dongpeng Lv, Validation were performed by Dan Zhu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data Availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figures

Figure 1

Optimized supercell configurations of CeO_2 and the $\text{CeO}_2(111)$ surface.

Figure 2

Top view of different adsorption sites on the $\text{CeO}_2(111)$ surface.

Figure 3

Adsorption of Hg on the $\text{CeO}_2(111)$ surface sites: (a) Ce top, (b) Ce-O bridge, (c) O top, and (d) O-O bridge.

Figure 4

Adsorption structures of AsH₃ on the CeO₂(111) surface: (a) Ce top, (b) Ce-O bridge, (c) O top, and (d) O-O bridge.

Figure 5

Adsorption of CO on the $\text{CeO}_2(111)$ surface: (a) Ce top, (b) Ce-O bridge, (c) O top, and (d) O-O bridge.

Figure 6

Reaction pathway and energy barriers for Hg^0 catalytic oxidation over the $\text{CeO}_2(111)$ surface.

Figure 7

Optimized IM, TS, and product geometries for the catalytic oxidation of Hg^0 on the $\text{CeO}_2(111)$ surface.

Figure 8

Reaction pathways and energy barriers for AsH₃ decomposition over the CeO₂(111) surface.

Figure 9

Optimized geometries of the IM and TS structures for AsH₃ decomposition over CeO₂(111) surface (pathway I).

Figure 10

Optimized geometries of IM and TS structures for AsH₃ decomposition over CeO₂(111) surface (pathway II).

Figure 11

Reaction pathway and energy barriers for the conversion of As-O bonds to products over CeO₂(111).

Figure 12

Optimized geometries of IM, TS, and products for the conversion of As-O bonds to the final products on CeO₂(111) surface.

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