Simultaneous catalytic oxidation of elemental mercury and arsine over CeO$_2$(111) surface: a density functional theory study

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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 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 CeO$_2$(111) surface, whereas CO is not, which is crucial for selective removal when CO is a desirable gas component. Furthermore, 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 the As–O bond seems the most plausible. Finally, the adsorbed As–O bond is further forms elemental As and As$_2$O$_3$. 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.

Keywords Ceria · Density functional theory · Elemental mercury · Arsine · Reaction mechanism

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. C1 chemical industry refers to the organic chemical industry process that syntheses chemical products or liquid fuels with the material containing one carbon atom as raw material, such as CO, CO$_2$, CH$_4$, CH$_3$OH, and HCHO. In order to improve the quality of subsequent C1 chemical products, it is necessary to carry out deep purification of tail gas. In addition, to CO, pollutants, including H$_2$S, elemental mercury (Hg$^0$), and arsine (AsH$_3$), are present in

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the phosphorus off-gas, which should be purified [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 Hg⁰ and AsH₃ 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 Hg⁰ and AsH₃ in yellow phosphorus off-gas limits its use as a raw material in other processes [5]. Therefore, Hg⁰ and AsH₃ removal technology is urgently needed.

Mercury in the gas phase mainly exists in three forms: particulate-bound mercury (Hg⁰), elemental mercury (Hg⁰), and oxidized mercury (Hg²⁺) [6]. Hg²⁺ is easily soluble in water, and Hg⁰ 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, Hg⁰ 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 (As₂O₅, As₂O₃, and arsenate) and reduced (AsH₃) species [5]. In yellow phosphorus off-gas, which is a highly reducing mixture, mercury mainly exists as Hg⁰, whereas arsenic mainly exists as AsH₃ [11]. Therefore, Hg⁰ and AsH₃ removal has become a research focus.

Currently, the main methods of Hg⁰ and AsH₃ 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 Hg⁰ and AsH₃. 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 Hg⁰ and AsH₃ removal efficiencies [21–24]. However, because of the high reactivity of CO, most catalysts will also react with this useful molecule. Furthermore, the use of separate equipment or catalysts to remove Hg⁰ and AsH₃ would result in significant capital investment for equipment and increase operating costs and process complexity. Therefore, selective catalysts for Hg⁰ and AsH₃ removal from reducing gas mixtures are required.

The key to developing selective catalysts for Hg⁰ and AsH₃ 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, CeO₂ contains the Ce³⁺/Ce⁴⁺ redox couple, which can vary from CeO₂ to Ce₂O₃ 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 CeO₂ has superior catalytic performance for the oxidation of Hg⁰, having 90% oxidation efficiency in simulated flue gas [25, 27]. Xie et al. [28] also used ceria to achieve a high AsH₃ 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 the CeO₂-modified SCR catalyst showed the highest Hg⁰ oxidation capacity [29]. In addition, in our previous work, we found that CeO₂ can oxidize Hg⁰ and AsH₃ 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 Hg⁰ and AsH₃ are converted to HgO, elemental As, and As₂O₃ on the catalyst surface, suggesting that Hg⁰ and AsH₃ are oxidized to these species by the lattice oxygen on the surface of the catalyst, and the mechanism of heterogeneous Hg⁰ and AsH₃ oxidation should follow the Mars–Maessen mechanism [5].

Nevertheless, few theoretical investigations of the mechanism of Hg⁰ and AsH₃ 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 CeO₂(111) surface. In this study, based on our previous work, we systematically and comprehensively studied the adsorption of Hg, CO, and AsH₃ on the CeO₂(111) surface using density functional theory (DFT) to assess the feasibility of the simultaneous catalytic oxidation of Hg⁰ and AsH₃ over CeO₂ 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 Hg⁰ and AsH₃ in reducing gas mixtures.

### Materials and methods

#### 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...
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 cutoff energy of 450 eV was used throughout the calculations. Furthermore, 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 ($E_{\text{ads}}$) describes the adsorption strength between the catalyst surface and corresponding gases, as given by Eq. (1) [35, 36].

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

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

**Atomic model of 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 Fig. 1a and

**Table 1** Adsorption energies and structural parameters for Hg$^0$ adsorbed on the CeO$_2$(111) surface

| Adsorption site    | $E_{\text{ads}}$/eV | $d_{\text{Hg-Ce}}$/Å | $d_{\text{Hg-O}}$/Å |
|-------------------|---------------------|-----------------------|----------------------|
| 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                |

![Fig. 1 Optimized supercell configurations of CeO$_2$ and the CeO$_2$(111) surface](image1)

![Fig. 2 Top view of different adsorption sites on the CeO$_2$(111) surface](image2)

![Table 1 Adsorption energies and structural parameters for Hg$^0$ adsorbed on the CeO$_2$(111) surface](table1)
b, and the constructed CeO2(111) surface model is shown in Fig. 1c and d. The optimized CeO2 supercell parameters were consistent with those from the literature (a = 10.98 Å, b = 10.98 Å, c = 16.78 Å).

Because of the exposure of Ce and O atoms on the CeO2(111) surface, there are four active sites on the CeO2(111) surface: O top, Ce top, O–O bridge, and Ce–O bridge, as shown in Fig. 2. By calculating the adsorption parameters at these four active sites, we can know the adsorption characteristics of pollutants on the catalyst surface, the specific calculation and model are shown in each chapter. A 2 × 2 × 1 supercell structure was used to study the adsorption of Hg0, AsH3, and CO on the CeO2(111) surface.

As mentioned in the “Materials and methods” section, a 10-Å-thick vacuum region was used to eliminate unphysical interactions between adjacent slabs [40].

**Results and discussions**

**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 (Hg$^0$, AsH$_3$, and CO) and the CeO$_2$ (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 Hg$^0$ 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 Hg$^0$ 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 Hg$^0$ adsorption. The distance between Hg and Ce in this adsorption mode is 3.241 Å.

Next, we studied the adsorption of AsH$_3$ on the CeO$_2$ (111) surface to understand the competitive adsorption of Hg$^0$ and AsH$_3$. The adsorption configurations of AsH$_3$ 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 AsH$_3$ adsorption on the CeO$_2$ (111) surface are shown in Fig. 4, and the corresponding adsorption energies and structural parameters are listed in Table 2. The bond length of arsine molecular looks short and results of a sigma-hole bonding interaction [42]. The adsorption of AsH$_3$ is energetically more favorable than that of Hg$^0$, and the most stable binding site for AsH$_3$ adsorption was the Ce top site. In this configuration, the distance between As and the Ce atom is 2.772 Å.

Finally, the adsorption of CO on the CeO$_2$ (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.

![Fig. 5 Adsorption of CO on the CeO$_2$ (111) surface: a Ce top, b Ce–O bridge, c O top, and d O–O bridge](image)

| Adsorption site     | $E_{ads}$/eV | $d_{AsH3-Ce}$/Å | $d_{AsH3-O}$/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          | $-1.271$     | $2.881$         | $2.718$        |
respectively. Importantly, all these values are positive, indicating that CO adsorption on the CeO$_2$(111) surface is unfavorable.

Therefore, in terms of the adsorption energies, on the CeO$_2$(111) surface, AsH$_3$ adsorption is most favorable, followed by Hg$^0$ adsorption; in contrast, CO adsorption is unfavorable. These results are consistent with our experimental observations that CeO$_2$ can adsorb and remove Hg$^0$ and AsH$_3$ in a strongly reducing atmosphere [5].

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 the 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

| Adsorption site     | $E_{ads}$/eV | $d_{CO-Ce}$/Å | $d_{CO-O}$/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        |

Fig. 6 Reaction pathway and energy barriers for Hg$^0$ catalytic oxidation over the CeO$_2$(111) surface

Fig. 7 Optimized IM, TS, and product geometries for the catalytic oxidation of Hg$^0$ on the CeO$_2$(111) surface
Fig. 8 Reaction pathways and energy barriers for AsH₃ decomposition over the CeO₂(111) surface.

Fig. 9 Optimized geometries of the IM and TS structures for AsH₃ decomposition over CeO₂(111) surface (pathway I).
was calculated to be 0.21 eV. Based on the first-principles calculation, we calculate that the activation energy of Hg to generate HgO on the CeO$_2$ surface is 0.09 eV (T = 0 K). According to Gibbs free energy formula, the free energy of generating HgO is negative at 423 K. When the temperature is 423 K, the reaction can proceed spontaneously under the drive of temperature. This result is consistent with our previous experimental observations.

**Mechanism of AsH$_3$ catalytic oxidation over the 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$_2$O$_3$. Furthermore, there are two possible pathways for AsH$_3$ decomposition on the CeO$_2$(111) surface. The combination of AsH$_3$ with O atoms of the CeO$_2$(111) surface followed by dehydrogenation or gradual dehydrogenation and the formation of bonds with O atoms from the 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 transition states for AsH$_3$ decomposition on the CeO$_2$(111) surface are shown in Fig. 9.

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**Fig. 10** Optimized geometries of IM and TS structures for AsH$_3$ decomposition over CeO$_2$(111) surface (pathway II)
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 AsOH$_2$ + 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 AsOH + 2H 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 the 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 CeO$_2$(111) surface.

Figure 10 presents the optimized geometries of the intermediates and transition states for AsH$_3$ decomposition on 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 AsH$_2$ + 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 AsH + 2H 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 → TS7 → IM9; imaginary frequency: \(-47.92 \text{ cm}^{-1}\)). This step has an energy barrier of 0.30 eV. Finally, the adsorbed \(As\) forms a bond with surface \(O\) spontaneously (IM9 → 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 \(AsH_3\) followed by the formation of a bond with an \(O\) atom of the \(CeO_2(111)\) surface seems the most plausible mechanism.

The length of the \(As-O\) bond in the \(As-O\) bond formed from \(AsH_3\) is 1.86 Å, which is similar to that in \(As_2O_3\), which may be the final product. Therefore, to determine the final products of the catalytic oxidation of \(AsH_3\), we carried out calculations on three \(As-O\) bonds on the \(CeO_2(111)\) surface. This resulted in the formation of elemental \(As\) and \(As_2O_3\). 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 the energy barrier to generate a new \(As-O\) bond, to form \(As=O\), and \(As=O\) intermediate (IM10 → TS8 → IM11; imaginary frequency: \(-74.24 \text{ cm}^{-1}\)). This process has an energy barrier of 0.18 eV. Next, a new \(As-O\) bond is formed to yield an \(As=O\), \(As=O\) intermediate (IM11 → TS9 → IM12; imaginary frequency: \(-93.23 \text{ cm}^{-1}\)) 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 \(As_2O_3\). The optimized geometries are shown in Fig. 12. The calculation results are consistent with our experimental observations [5]. Thus, overall, \(AsH_3\) is dehydrogenated stepwise and then forms bonds with \(O\) on the \(CeO_2(111)\) surface to yield elemental \(As\) and \(As_2O_3\).

**Conclusions**

In this work, we systematically studied the adsorption and catalytic oxidation of \(Hg^0\) and \(AsH_3\) on the \(CeO_2(111)\) surface. Comparing the adsorption energies and the adsorption configurations of \(Hg^0\), \(AsH_3\), and \(CO\), we found that the most stable binding sites for \(Hg^0\) and \(AsH_3\) 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, \(AsH_3\) adsorption is most favorable, followed by that of \(Hg^0\), whereas \(CO\) adsorption on \(CeO_2(111)\) is unfavorable. This result suggests that \(CeO_2\) could selectively adsorb and remove \(Hg^0\) and \(AsH_3\) in strongly reducing gas mixtures, such as yellow phosphorus off-gas. In addition, the reaction mechanisms were investigated using DFT calculations. The catalytic oxidation of \(Hg^0\) 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, \(AsH_3\) is gradually dehydrogenated and forms bonds with an \(O\) atom of the \(CeO_2(111)\) surface to yield the \(As-O\) bond. Finally, the \(As-O\) bonds are converted to elemental \(As\) and \(As_2O_3\).

The results of this study provide an understanding of \(Hg^0\) and \(AsH_3\) adsorption and catalytic oxidation on the \(CeO_2\) surface, and we conclude that ceria is a promising catalyst for the removal \(Hg^0\) and \(AsH_3\) from strongly reducing off-gases.

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**Author contribution** Yingjie Zhang: methodology, writing—original draft preparation, investigation; Hujuan Yu: writing—reviewing and editing; Xueqian Wang: conceptualization, funding acquisition; Langlang Wang: writing—reviewing and editing; Yuancheng Li: investigation, funding acquisition; Dongpeng Lv: data curation; Dan Zhu: validation; Chunmei Tian: writing—reviewing and editing.

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**Declarations**

**Conflict of interest** The authors declare no competing interests.

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