Exploring PtSO$_4$ and PdSO$_4$ phases: an evolutionary algorithm based investigation

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Metal sulfate formation is one of the major challenges to the emissions aftertreatment catalysts. Unlike the incredibly sulfation prone nature of Pd to form PdSO$_4$, no experimental evidence exits for the PtSO$_4$ formation. Given the mystery of nonexistence of the PtSO$_4$, we explore the PtSO$_4$ using a combined approach of evolutionary algorithm based search technique and quantum mechanical computations. Experimentally known PdSO$_4$ is considered for the comparison and validation of our results. We predict many possible low-energy phases of the PtSO$_4$ and PdSO$_4$ at 0K, which are further investigated under wide range of temperature-pressure conditions. An entirely new low-energy (tetragonal $P4_2/m$) structure of the PtSO$_4$ and PdSO$_4$ is predicted, which appears to be the most stable phase of the PtSO$_4$ and a competing phase of the experimentally known monoclinic $C2/c$ phase of PdSO$_4$. Phase stability at finite temperature is further examined and verified by free energy calculations of sulfates towards their possible decomposition products. Finally, temperature-pressure phase diagrams are computationally established for both PtSO$_4$ and PdSO$_4$.

1 Introduction

Sulfation (i.e. metal sulfate formation) of noble metal based catalysts has been a serious problem to automotive emissions aftertreatment systems. It is well established that Pd is extremely susceptible towards sulfation (i.e., the PdSO$_4$ formation) in the highly oxidizing and sulfating environment typically experienced by the aftertreatment catalysts. Unlike the easily formed sulfate PdSO$_4$ under catalytically relevant conditions, no experimental evidence is available for the existence of PtSO$_4$ under any circumstances. Despite being a member of the same group of the Periodic Table, an intriguing fact of non-existence of PtSO$_4$ remains as a puzzle and an unexplored territory. A question arises why PtSO$_4$ does not exist and what makes PtSO$_4$ different from PdSO$_4$? Answers to these questions may reveal the underlying mystery behind sulfation resistant phenomena of Pt and, in turn, provide some guidance for future design of sulfur resistant catalysts materials.

An experimental investigation based reaction pathway analysis suggested that the PdSO$_4$ formation is primarily due to the interaction between SO$_3$ and metal oxide (i.e., PdO) in the catalytically relevant temperature and pressure conditions. Under similar experimental conditions, no PtSO$_4$ formation has been observed. In a recent study based on the first principle computations, Derzsi et al. suggested that the structure of PtSO$_4$ should be similar to that of PdSO$_4$ while assuming a similar nature of metal oxides (i.e. PdO and PtO) of Pd and Pt. Our recent work on Pt and Pd surfaces utilizing the first-principles thermodynamics suggested that the PtSO$_4$ formation is indeed favored even at lower temperature pressure conditions; however, the PtSO$_4$ formation may be favorable only at elevated pressure conditions. This outcome points out a direction for further investigations of the Pt and Pd sulfates under a wide range of temperature and pressure regimes, for which comprehensive information on the possible structural phases is required. Furthermore, PdSO$_4$ is stable towards decomposition to metal oxide (PdO) and sulfur oxides (SO$_2$/SO$_3$) below $\sim$650°C which suggests that once the stable sulfate is formed, it is difficult to desulfate the catalysts. Unfortunately, such information is missing for PtSO$_4$ and needs an attention.

Our work is premised on the aforementioned mystery of contrasting behavior of Pt and Pd metals towards sulfation. We extensively explore the possible low-energy structures of the yet-to-be synthesized PtSO$_4$ and the known PdSO$_4$ using evolutionary algorithm-based method Universal Structure Predictor: Evolutionary Xtalloraphy (USPEX). Stability of the predicted low-energy structures are assessed by the evaluation of Gibbs free energy over a wide temperature-pressure range, fully considering the vibrational contributions calculated within the harmonic approximation. Furthermore, we investigate the stability of the predicted structures towards decomposition to their possible products. In this work, most notably we predict a tetragonal $P4_2/m$ structure (no. 84) to be the lowest in energy for both PtSO$_4$ and PdSO$_4$. Interestingly, we find that the experimentally-known monoclinic $C2/c$ phase (no. 15) of PdSO$_4$ is energetically competing with the newly identified $P4_2/m$ phase. Moreover, we construct phase diagrams of the PtSO$_4$ and PdSO$_4$ over a range of temperature and pressure which shows the stability of various sulfate phases.

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### 2 Methods

Possible stable structures of PdSO$_4$ and PtSO$_4$ are searched using an evolutionary search technique embodied in USPEX code\cite{13,14}. The code/method, predicts the crystal packing from only a knowledge of chemical species, compositions, or the molecular geometries, has met tremendous success in correctly identifying and predicting the crystal structures of various classes of systems (bulk crystals,\cite{15,16} nanoclusters,\cite{17} 2D crystals,\cite{18} surfaces,\cite{19} and new polymers\cite{20,21}). In this work, we explored the structural space of PtSO$_4$ and PdSO$_4$, with a fixed stoichiometric composition, allowing up to four formula units per unit cell. The energy ordering, lattice parameters, and the electronic structures of the identified phases are determined within the framework of density functional theory (DFT) using the all electron projector augmented wave method\cite{22,23} as implemented in Vienna Ab initio Simulation Package (VASP) code.\cite{24,25} Our DFT calculations are performed within the generalized gradient approximation using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional.\cite{26,27} It is worth mentioning that the energy ordering is invariant with respect to the choice of the XC functional. All the plane waves with kinetic energy up to 500 eV was used in our basis set. To sample the Brillouin zone, we employed Monkhorst-Pack k-point mesh producing the convergence within 1 meV per formula unit. The atomic positions are optimized by relaxing all the atoms until the Hellman–Feynman forces become less than 0.01 eV/Å. The density of states (DOS) is calculated by the linear tetrahedron method with Blöchl corrections.

Dynamical stability of all the selected structural candidates is confirmed by the phonon frequency spectra calculated using the finite-displacement approach as implemented in the PHONOPY code.\cite{29,30} To establish the stability of the predicted phases at finite temperature and pressure, relevant thermodynamic properties were evaluated from the computed phonon band spectra. FullProf suite\cite{31} was used to simulate the X-ray diffraction patterns.

### 3 Results and discussion

#### 3.1 Low-energy structures of PdSO$_4$ and PtSO$_4$

The evolutionary algorithm based search for ground-state phases of PdSO$_4$ and PtSO$_4$ resulted in a large number of possible low-energy structures. Total six such low-energy structures (in right panel) for both cases (i.e. PtSO$_4$ and PdSO$_4$) and their relative energy (in left panel) are shown in the Figure 1. The $P4_2/m$ phase is predicted to be the most stable phase of both PdSO$_4$ and PtSO$_4$. The experimentally known $C2/c$ structure\cite{32} of PdSO$_4$ is energetically very similar (within the computational error limit) as a competing phase. However, the $P4_2/m$ phase of PtSO$_4$ is significantly lower in energy than the second most stable phase $C2/c$. More specifically, the energy difference between the $C2/c$ and the $P4_2/m$ structures is $\sim 8$ meV/atom and $\sim 21$ meV/atom for PdSO$_4$ and PtSO$_4$, respectively. Orthorhombic $Ibam$ (no. 72), tetragonal $P4/n$ (no. 85) phases of both are relatively similar in energetics, notably the orthorhombic $I\bar{2}2$ (no. 23), and tetragonal $I\bar{4}$ (no. 82) structures of PtSO$_4$ are less stable compared to the same structures of PdSO$_4$. Structural information (lattice parameters, atomic coordinates etc.) for all the phases of PdSO$_4$ and PtSO$_4$ shown in the supplementary information.
in Figure 1 is given in the Supporting Information (see Table S1).

The predicted low-energy structures of both sulfates are morphologically similar. Each structure consists of tetrahedral SO₄ groups, where O atoms are associated to four different SO₄ tetrahedra coordinating the Pd atoms in a plane. The local chemistry at the anionic site, the topology and the connectivity of the crystal networks are also qualitatively similar in both sulfates. In general, these six structures can be classified into two groups. The first structure type, with a non-layered 3-D network, contains oxygen atoms from the SO₄ unit which act as a bridge (for example: P₄/m̅, C2/c, and I̅2̅2̅2 phases) linking metal atoms. The second structure type involves some two-dimensional motifs with isolated layers of Pd/Pt and SO₄ tetrahedra (for example: Ibam, P₄/n, and I222 phases).

We further analyzed the selected low-energy structures by simulating the X-ray diffraction (XRD) patterns. In Figure 2 (top panels), we show the XRD simulations of C2/c and P42/m phases of PdSO₄ along with the available experimental XRD data of C2/c phase. In bottom panels (Figure 2), we show the XRD simulations of our predicted C2/c and P42/m phases along with the suggested C2/c phase of PtSO₄ by Derzsi et al. Overall, the simulated peaks in XRD plot are in good agreement with the available experimental data. The additional XRD simulations (of the other predicted phases) are given in the Supporting Information S2.

3.2 Dynamical and thermodynamic stabilities

Next, we examined the dynamical stability of all predicted low-energy structures of PtSO₄ and PdSO₄ using the calculated phonon band structures. No imaginary modes exist throughout the Brillouin zones of these structures, demonstrating that they are dynamically stable. For illustration, we show in Fig. 3 the phonon spectra and the phonon density of states g(ω) we calculated for the lowest-energy structures of each compound, i.e., the P42/m structure of PtSO₄ and the C2/c structure of PdSO₄. Similar information for all other predicted structures can be found in the Supporting Information S3.

The phonon spectra of these structures, calculated at 0K, allow estimating the vibrational contribution F_vib(T) to the Gibbs free energy G(P,V,T) = E_DFT + F_vib(T) + PV within the harmonic approximation via

\[ F_{\text{vib}}(T) = r k_B T \int_0^\infty d\omega g(\omega) \ln \left( \frac{\hbar \omega}{2 k_B T} \right), \]  

where, r is number of degrees of freedom in the unit cell, k_B is the Boltzmann’s constant, \( \hbar \) is the reduced Planck’s constant, and g(ω) is the normalized phonon density of state at
Fig. 4 Gibbs free energies with entropic contributions, $G$ calculated at $T = 0K$, $T = 300K$, $T = 700K$, and $T = 1000K$ for the identified low-energy structures of PdSO$_4$ (panel a) and PtSO$_4$ (panel b) are shown as functions of pressure $P$. Data is given by symbols while curves are guides to the eye.

frequency $\omega$. For hard crystalline materials, the method provides a good way to access their thermodynamic stability and typically yields an excellent agreement with experimental data (see, for example, Ref. \cite{33}).

Our calculations for $G(P,V,T)$ are summarized in Figure 4. Results suggest that the $P4_{2}/m$ phase of PtSO$_4$ is the thermodynamically stable at low pressures and over the temperature range considered. In the case of PdSO$_4$, the $C2/c$ structure (which is experimentally established\cite{32}) is very slightly less stable than the $P4_{2}/m$ structure by $\sim 2$ meV at low pressures and temperatures. According to our calculations, the $C2/c$ phase becomes thermodynamically stable at above 700K. We note that the energy difference between these structures are comparable within the accuracy of DFT and both structures are energetically competing phases of PdSO$_4$. The formation of the $C2/c$ phase, which is observed even at low temperatures conditions, may be driven by kinetics, which is well-known under the empirical Ostwald’s steps rules in crystal nucleation.

Both PdSO$_4$ and PtSO$_4$ undergo several structural phase transitions at higher pressures. For PdSO$_4$, the orthorhombic $Ibam$ phase is stable within a wide range of pressure from $\sim 10$ to $\sim 80$ GPa before transforming to the tetragonal $I\bar{4}$ phase. The phase boundaries depend weakly on temperature. While the $Ibam$ phase is clearly thermodynamically most stable between 10 and 80 GPa, the monoclinic $C2/c$ and the tetragonal $P4/n$ are energetically competing with the $I\bar{4}$ phase above 80 GPa. The energy differences between these phases are small compared to the thermal energy $k_BT$, especially at the high limit of $T$. Unlike the PdSO$_4$, the $C2/c$ phase of PtSO$_4$ is more stable only at high temperature ($> 700K$) and slightly elevated pressure ($> 10$ GPa) conditions while the $Ibam$ phase is stable at lower temperatures ($< 700K$) and elevated pressure (10–60 GPa) conditions. The transition between the $Ibam$ phase to either the $I\bar{4}$ or the $C2/c$ phase occurs at roughly around 60 GPa. For both PdSO$_4$ and PtSO$_4$, the $I222$ phase is unstable over the whole range of pressure examined.

Utilizing the information about the phase stability from Figure 4, we constructed the phase diagrams of both sulfates from the calculated free energy $G(P,V,T)$ as shown in Figure 5. The phase diagrams display a map of the stable phases over the range of $T$-$P$ conditions. Most importantly, we observed that the tetragonal $P4_{2}/m$ is a sole candidate for atmospheric pressure and relevant temperature pressure conditions. However, $P4_{2}/m$ and $C2/c$ phases are the important phases in the similar conditions. Furthermore, the $Ibam$ phase dominates the
10–60 GPa region for both cases, which could be an interest of exploration for the high pressure applications.

While experimental studies suggest that PdSO₄ decomposes above ~900K, estimation of free energy of reaction (∆G) over a range of temperature allows us to evaluate the thermodynamic stability (reaction feasibility) of the compound towards decomposition to its products. The feasibility of a reaction depends on the sign of ∆G, which is equal to ∆H − T∆S, where ∆H is the change in enthalpy and ∆S is the change in entropy. The ∆G of the reaction can be expressed as:

$$\Delta G = \sum_{i=1}^{n} G_{\text{products}} - \sum_{i=1}^{n} G_{\text{reactants}} \quad (2)$$

In this work, we considered the decomposition reaction of Pd(or Pt)SO₄ towards their respective most stable metal oxides and sulfur oxide species [i.e. Pd(or Pt)SO₄ → Pd(or Pt)O + SO₃]. For example, the computed ∆G values at 300K were ~60 kJ/mol and ~40 kJ/mol for PdSO₄ and PtSO₄, respectively. Furthermore, we evaluated the free energy of the decomposition of the sulfates to their respective elemental species (i.e. Pd (or Pt) SO₄ → Pd (or Pt) + S + 2O₂). The computed ∆G values were in the range of ~500 kJ/mol at 300K.

Results suggest that PdSO₄ is stable towards decomposition to PdO and SO₃ below 775K whereas PtSO₄ stability towards PtO and SO₃ remains below 650K. Similarly, PdSO₄ is stable towards the decomposition to the elemental components below 870K whereas PtSO₄ is stable below 800K. In general, our calculations show that PdSO₄ is more stable than PtSO₄ towards decomposition for a particular temperature. Our results are in good agreement, given the computational error range in energetics, with the available experimental results of PdSO₄ decomposition stability. Furthermore, synthesis of PtSO₄ seems feasible in the future given the kinetic barriers are easy enough to cross. The free energy (∆G) versus temperature (T) plot is given in Supporting Information S4.

To further confirm whether these sulfates are stable or not with respect to the pool of all possible product species, a linear programming (LP) algorithm [26,27] has been employed. Here, a Pd(or Pt)SO₄ compound is considered to be stable when ∆E (the DFT energy relative to the best outcome from the LP) is negative. The energy difference, ∆E, can thus be written as

$$\Delta E = \text{Pd(or Pt)SO}_4 - \min_{i=1}^{n} c_i P_i \quad (3)$$

where $P_i$ represents all the possible stable chemical species (i.e. for PdSO₄: Pd, PdO, SO₃, SO₂, SO, S, and O₂; for PtSO₄: Pt, PtO₂, PtO, SO₃, SO₂, SO, S, and O₂). For example, the equation for PdSO₄ becomes $\Delta E = \text{PdSO}_4 - \min(c_1\text{Pd} + c_2\text{PdO} + c_3\text{SO}_3 + c_4\text{SO}_2 + c_5\text{SO} + c_6\text{S} + c_7\text{O})$. Then, the LP problem is solved with the constraints

$$\sum_{i} a_i c_i = 1, \sum_{i} b_i c_i = 1, \text{ and } \sum_{i} c_i = 4 \quad (4)$$

where $a_i$, $b_i$, and $c_i$ represent Pt(or Pd), S, and O content of a species, respectively. Above constraints ensure the correct stoichiometry of Pd(or Pt)SO₄ and with

$$c_i \geq 1 \quad (5)$$

which warrants that only the references containing Pt(or Pd), S, or O are taken into account. With all DFT computed energies of the species, we obtained all the optimized $c_i$ and $\Delta E$ for each case. Consistent with our free energy of reaction analysis, negative $\Delta E$ values (i.e. ~0.87 eV and ~0.70 eV for PdSO₄ and PtSO₄, respectively) were obtained, which confirmed the stability of the sulfates. Interestingly, we obtained mono-metallic oxides (PdO and PtO in the case of PdSO₄ and PtSO₄, respectively) and SO₃ as possible decomposition products, consistent with our reaction free energy analysis, and unity (as expected) for all $c_i$ values.

### 3.3 Electronic structures

We investigated the electronic structures of all low-energy phases of PdSO₄ and PtSO₄ by computing the total density of states. Overall, our results show no significantly different behavior between the phases of both sulfates. For better understanding the DOS can be divided into three main groups. First, the lower valence bands (between ~2 eV and ~4 eV) originate due to mixing of the valence $d$ and $p$ states of Pd(or Pt) and the O atoms. In this region, Pd(or Pt) ($d$) bands are found to be highly resonant with the O ($p$) bands. We also noticed that some pronounced mixing between the segments of O ($p$) bands lying above and below the valence Pd(or Pt) ($d$)
bands. Second, in the vicinity of the Fermi level the valence-band maximum are dominated by Pd(or Pt) (d) states. Third, the bottom of the conduction band consists 3p states of S and O (2p) states. Further detail can be found in the Supporting Information S5.

4 Conclusions

In summary, we explored the mystery of PtSO$_4$ non-existence using evolutionary algorithms based method and the first principles computations. We considered the known PdSO$_4$ for the comparison and validation of our approach. Many low-energy structures are predicted and analyzed for the stability in a wide range of temperature and pressure conditions. We identify a new stable tetragonal P4$_2$/m structure for both metal sulfates. We predicted that the P4$_2$/m phase is the most stable phase of PtSO$_4$ and a competing structure with monoclinic C2/c phase of PdSO$_4$. Based on the computed Gibbs free energies, we constructed phase diagrams which provide reliable information about the phases stability, phase transition, and their boundaries in a wide range of temperature and pressure conditions. Phase diagrams confirmed the existence of experimentally observed monoclinic C2/c phase of PdSO$_4$ at the ambient conditions; however, this phase may not be seen in the case of PtSO$_4$ in similar conditions. Nonetheless, Ibam phase remains one of the promising stable phase for both cases at high pressure conditions. Both sulfates were stable towards decomposition to their possible products well above the room temperature, which also suggests the possibility of PtSO$_4$ synthesis in the future. In general, we provide a detailed information on the phases and their stability of PdSO$_4$ and PtSO$_4$ which can be helpful to understand the sulfating nature of Pd and design/scan promising new sulfur resistant materials.

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Supplementary Information

Electronic Supplementary Information (ESI) available: Structural information of PtSO$_4$ and PdSO$_4$ are shown in S1, XRD patterns of the predicted structures are shown in S2, the phonon density of states are shown in S3, free energy diagram is given in S4, and electronic density of states are shown in S5 of the Supplementary Information.

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