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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 0 K, 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 Gibbs 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.\textsuperscript{1–6} 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.\textsuperscript{7} Despite being a member of the same group of the Periodic Table, an intriguing fact of non-existence of PdSO$_4$ 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 reason behind the 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.\textsuperscript{8} Nevertheless, no PtSO$_4$ formation has been observed under similar experimental conditions.\textsuperscript{9,10} A recent first-principles computation based study 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.\textsuperscript{7} Using first-principles thermodynamics we have recently predicted that the PdSO$_4$ formation is indeed favored even at lower temperature pressure conditions; however, the PtSO$_4$ formation may be favorable only at elevated pressure conditions.\textsuperscript{11} 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$_3$/SO$_2$) below $\sim 650 \degree$C\textsuperscript{12} 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).\textsuperscript{13,14} The thermodynamic 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. From free energies calculations, we propose the temperature-pressure phase diagrams for PdSO$_4$ and PtSO$_4$, predicting the

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stable phases of the sulfates at high temperatures and/or high pressures.

2 Methods

Structural phases of compressed matters can now be effectively predicted and discussed at elevated pressures by many state-of-the-art computational methods, mostly at the level of first principles. In this work, possible stable structures of PdSO\(_4\) and PtSO\(_4\) were searched using the evolutionary search technique embodied in USPEX code. This code/method, designed to predict 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, nanoclusters, 2D crystals, surfaces, and recently for polymers). In this work, we explored of the low-energy configurational spaces of up to four formula units of PdSO\(_4\) and PtSO\(_4\) per primitive cell, i.e., \(Z \leq 4\). Structures with \(Z > 4\) (for example, experimentally observed low temperature \(Z = 16\) structure of PdSO\(_4\)) are not considered, and hence, sets a limitation of this work.

Our first-principles calculations were performed within the framework of density functional theory (DFT) using the projector augmented wave method as implemented in Vienna Ab initio Simulation Package (VASP). While the generalized gradient approximation Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional was used throughout this work, the energy ordering of the identified structures were confirmed to be invariant with the PBEsol XC functional. A basis set of plane waves with kinetic energy up to 600 eV was used to represent the Kohn-Sham orbitals while the Brillouin zones were sampled by well-converged Monkhorst-Pack \(k\)-point meshes, i.e., no less than \(7 \times 7 \times 7\). Convergence in optimizing the structures was assumed when the Hellman-Feynman forces become less than 0.01 eV/Å.

We calculated the densities of states (DOS) of the identified structures by the linear tetrahedron method with Bloch corrections. For examining their dynamical stability, the phonon frequency spectra calculated using the finite-displacement approach as implemented in the PHONOPY code. To establish the stability of the predicted phases at finite temperatures and pressures, relevant thermodynamic properties were evaluated within the harmonic approximation from the computed phonon band spectra. FULLPROF suite was used to simulate the X-ray diffraction patterns.

3 Results and discussions

3.1 Low-energy structures of PdSO\(_4\) and PtSO\(_4\)

Our evolutionary algorithm based search for low-energy structures of PdSO\(_4\) and PtSO\(_4\), performed at zero pressure \((P = 0\) GPa), returned numerous possible candidates. Eight of them (six \(Z = 2\) and two \(Z = 4\) structures), which are lowest in energy for both PtSO\(_4\) and PdSO\(_4\), and their energetic information are shown in Fig. 1. Of the two common thermodynamically most stable structures of these sulfates, one is described by the tetragonal \(P4_2/m\) space group (no. 84) while the other belongs to the monoclinic \(C2/c\) space group (no. 15). It is worth noting that the \(P4_2/m\) structure can also be obtained by substituting Pd/Pt into the Ag sites of the \(Pt\) \((Z = 2)\) structure of AgSO\(_4\). On the other hand, the \(C2/c\) structure, which was experimentally known for PdSO\(_4\), is similar to that discussed earlier by Derzsi et al. We then found that the \(C2/c\) structure of PdSO\(_4\) is higher in energy than the \(P4_2/m\) structure by \(\approx 8\) meV/atom, falling within the uncertainty of DFT in calculating energies, while for PtSO\(_4\), this energy difference is considerably larger, being roughly 20 meV/atom. In case of
PdSO$_4$, a $Z = 16$ structure (Pc or P/2c) was also observed\cite{22} but its crystallographic information has yet been resolved. The fact that both C2/c and Pc (or P2/c) exist implies that they are energetically competing with the P4$_2$/m structure in this work. The orthorhombic Ibam (no. 72) and the tetragonal P4/n (no. 85) structures of both PdSO$_4$ and PtSO$_4$ are relatively similar in energy, residing at $\gtrsim 50$ meV/atom above the P4$_2$/m. Two $Z = 4$ triclinic structures examined, namely $\alpha$-P1 and $\beta$-P1 (both no. 1), are about 30 – 50 meV/atom above the P4$_2$/m structure. The last two structures, i.e., I222 (orthorhombic, no. 23) and I4 (tetragonal, no. 82), are about 75 – 100 meV/atom higher than the P4$_2$/m structure. We note that these structures are slightly below the C2/c ($Z = 16$) structure recently determined\cite{32} for AgSO$_4$. This energy ordering remains essentially unchanged when PBEsol and LDA were used (also see Fig. 1). Crystallographic information of the predicted structures is given in the Supporting Information (see Table S1).

The predicted low-energy structures of both sulfates consist of tetrahedral SO$_4$ groups, where O atoms are associated to four different SO$_4$ tetrahedra coordinating the Pd/Pt atoms on 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 eight structures can be classified into two groups. The first structure type, with a non-layered 3-D network, contains oxygen atoms from the SO$_4$ unit which act as a bridge (for example: P4$_2$/m, C2/c, I4, and $\beta$-P1 phases) linking metal atoms. The second structure type involves some two-dimensional motifs with isolated layers of Pd/Pt and SO$_4$ tetrahedra. The remaining four structures, i.e., Ibam, P$_4$/n, I222, and $\alpha$-P1 phases, belong to this class.

We further analyzed the selected low-energy structures by simulating the X-ray diffraction (XRD) patterns. In Fig. 2 (top two panels), we show the XRD patterns simulated for the C2/c and P4$_2$/m structures of PdSO$_4$ along with the available experimental XRD data of the C2/c phase.\cite{33} In the bottom two panels of Fig. 2, we show the XRD patterns simulated for our predicted C2/c and P4$_2$/m phases. Overall, the simulated XRD patterns are in good agreement with the available experimental data.\cite{33} The additional simulated XRD patterns (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 the predicted 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 \( g(\omega) \) we calculated for the lowest-energy structures of each compound, i.e., the \( P4_2/m \) and \( C2/c \) structures. Similar information for all other predicted structures can be found in the Supporting Information S3.

The phonon spectra of these structures, calculated at 0 K, allow estimating the vibrational contribution \( F_{\text{vib}}(T) \) to the Gibbs free energy \( G(P,V,T) = E_{\text{DFT}} + F_{\text{vib}}(T) + PV \) within the harmonic approximation via

\[
F_{\text{vib}}(T) = r k_B T \int_0^\infty d\omega g(\omega) \ln \left[ 2 \sinh \left( \frac{\hbar \omega}{2 k_B T} \right) \right], \tag{1}
\]

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 \( g(\omega) \) is the normalized phonon density of state at frequency \( \omega \). In addition, the enthalpy \( E_{\text{DFT}} + PV \) was calculated by slowly optimizing the investigated structures under gradually increasing pressure, starting from \( P = 0 \) GPa. For hard crystalline materials, this method typically leads to an excellent agreement with experimental data.³⁴

The calculated free energies \( G(P,V,T) \) are summarized in Fig. 4, suggesting that the \( P4_2/m \) phase of PtSO₄ is thermodynamically stable at low pressures. Within this regime, the \( C2/c \) structure of PdSO₄ (which is experimentally established²²) is different from the \( P4_2/m \) structure by no more than \( \pm 2 \) meV/atom at low and high temperatures. Therefore, these two phases are considered to coexist at low pressures. The formation of the \( C2/c \) phase, which is observed even at low temperatures conditions, may be driven by kinetics, known under the empirical Ostwald’s steps rules in crystal nucleation.

Both PdSO₄ and PtSO₄ undergo several structural phase transitions at elevating pressures. For PdSO₄, the orthorhombic \( Ibam \) phase is stable between \( \sim 10 \) and \( \sim 60 \) GPa before transforming to the triclinic \( \beta-P1 \) phase. The \( Ibam \)-to-\( \beta-P1 \) phase boundary depends very weakly on temperature. Unlike PdSO₄, the \( C2/c \) phase of PtSO₄ is thermodynamically stable only at high temperature (\( \gtrsim 700 \) K) and intermediate pressure (\( 10 - 30 \) GPa) conditions while the \( Ibam \) phase is stable at lower temperatures (\( \lesssim 700 \) K) and elevated pressure (\( 10 - 60 \) GPa) conditions. The transition between the \( Ibam \) phase to the \( I4 \) phase occurs at roughly around \( 60 \) GPa.

Using the calculated free energies \( G(P,V,T) \) (as shown in Fig. 4), we constructed the temperature-pressure phase diagrams of both sulfates and show them in Fig. 5. The phase diagrams display a map of the stable phases over the range of \( T-P \) conditions. Most importantly, we observed that for PdSO₄, both the tetragonal \( P4_2/m \) and the monoclinic \( C2/c \) phases coexist at atmospheric pressures while for PtSO₄, the \( P4_2/m \) phase is the sole candidate at the same conditions. Furthermore, the \( Ibam \) phase dominates the \( 10 - 60 \) GPa region.
4 is stable towards the decomposition to the elemental compounds. In general, our calculations show that PdSO$_4$ is stable towards the sulfates in realistic temperature ($4 \rightarrow P$) conditions. The change in enthalpy and $\Delta S$ is the change in entropy. The free energy ($\Delta G$) of the reaction can be expressed as:

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

In this work, we considered the decomposition reaction of Pd(Or Pt)SO$_4$ towards their respective most stable metal oxides and sulfur oxide species [i.e. Pd(Or Pt)SO$_4 \rightarrow$ Pd(Or Pt)O + SO$_3$]. For example, the computed $\Delta G$ values at 300 K were $\sim -60$ kJ/mol and $\sim -40$ kJ/mol for PdSO$_4$ and PtSO$_4$, respectively. Furthermore, we evaluated the free energy of the decomposition of the sulfates to their respective elemental species (i.e. Pd or Pt) SO$_4 \rightarrow$ Pd(Or Pt) + S + 2O$_2$. The computed $\Delta G$ values were in the range of $\sim -500$ kJ/mol at 300 K. Results suggest that PdSO$_4$ is stable towards decomposition to PdO and SO$_3$ below 775K whereas PtSO$_4$ stability towards PtO and SO$_3$ remains below 650 K. Similarly, PdSO$_4$ is stable towards the decomposition to the elemental components below 870 K whereas PtSO$_4$ is stable below 800 K. Furthermore, we computed the $\Delta G$ for the reaction Pd(Or Pt)SO$_4 \rightarrow$ Pd (or Pt)S + 2O$_2$, which further supports the stability of the sulfates in realistic temperature (< 700 K) and pressure conditions. In general, our calculations show that PdSO$_4$ is more stable than PtSO$_4$ 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 PdSO$_4$ decomposition stability. Furthermore, synthesis of PtSO$_4$ seems feasible in the future given the kinetic barriers are easy enough to cross. The free energy ($\Delta G$) versus temperature ($T$) plot is provided in Supporting Information (S4, Figure S3).

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$^{15,36}$ has been employed. Here, a Pd(Or Pt)SO$_4$ compound is considered to be stable when $\Delta E$ (the DFT energy relative to the best outcome from the LP) is negative. The energy difference, $\Delta E$, can thus be written as:

$$\Delta E = Pd(Or Pt)SO_4 - \min \sum_{i=1}^{n} c_i P_i,$$  (3)

where $P_i$ represents all the possible stable chemical species (i.e. for PdSO$_4$: Pd, PdO, PdS, SO, SO$_2$, SO, S, and O$_2$; for PtSO$_4$: Pt, PtO$_2$, PtO, PtS, SO$_3$, SO$_2$, SO, S, and O$_2$). For example, the equation for PdSO$_4$ becomes $\Delta E = PdSO_4 - \min(c_1 Pd_{a1} + c_2 Pd_{a2} O_{o2} + c_3 Pd_{b1} S_{b3} + c_4 Pb_{b4} O_{b4} + c_5 Pb_{b5} O_{b5} + c_6 Pb_{b6} O_{b6} + c_7 Pb_{b7} + c_8 Pb_{b8} O_{b8})$. Then, the LP problem is solved with the constraints

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

where $a_i$, $b_i$, and $c_i$ represent Pt(Or Pd), S, and O content of a species, respectively. Above constrains ensure the correct stoichiometry of Pd(Or Pt)SO$_4$ and with

$$c_i \geq 1,$$  (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 PdSO$_4$ and PtSO$_4$, respectively) were obtained, which confirmed the stability of the sulfates. Interestingly, we obtained mono-metallic oxides (PdO and PtO in the case of PdSO$_4$ and PtSO$_4$, respectively) and SO$_3$ 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 PdSO$_4$ and PtSO$_4$ 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 related to nonexistence of PtSO₄ using first-principles thermodynamics combined with the evolutionary algorithms based method. Our approach is validated by also studying the experimentally known phases of PdSO₄. Many low-energy structures are predicted and analyzed for the stability in a wide range of temperature and pressure conditions. At low pressures, we identify a monoclinic PdSO₄ structure (of the AgSO₄ type) which appears to be the thermodynamically most stable phase of PtSO₄. In case of PdSO₄, this phase is predicted to coexist with the experimentally known C2/c phase. These sulfates are also predicted to undergo several phase transitions at elevated temperatures and/or pressures. Based on the computed Gibbs free energies, we constructed phase diagrams which provide such the reliable information about the phases stability, the phase transition, and their boundaries up to 100 GPa and 1000 K. The phase diagrams confirmed the existence of experimentally observed monoclinic C2/c phase of PdSO₄ at the ambient conditions; however, this phase may not be seen in the case of PtSO₄ 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 PtSO₄ synthesis in the future. In general, we provide a detailed information on the phases and their stability of PdSO₄ and PtSO₄ 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 PtSO₄ and PdSO₄ 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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