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A comparative study of the interaction of platinum with group 4A (germanium, tin and lead) porphyrins

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Abstract

Because of its vast number of applications and high price many studies have been made on how to reduce the amount of platinum in catalysts. One method includes dispersing platinum nanoparticles in porous support materials. But electrically conductive carbon-based support materials—needed for fuel cell electrodes—permit nanoparticles to migrate and form larger clusters, leading to reduced catalytic activity over time. To find a solution to this problem, we modelled the interaction of group 4A metal porphyrins (germanium (II) porphyrin (GePor), tin (II) porphyrin (SnPor) and lead (II) porphyrin (PbPor)) with platinum (Pt) using density functional theory. We showed that platinum can bond strongly on both germanium porphyrin and tin porphyrin. More importantly, valence Pt d-orbital characteristics dominate their HOMO and HOMO-1. Our study indicates that dispersing Pt as individual atoms on a SnPor and GePor surface is a good way to minimize platinum load in carbon-based reduction catalysts for reactions involving mainly the HOMO and HOMO-1 of Pt, of which the oxygen reduction reaction in fuel cells is an example.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Platinum (Pt) is important because of its versatile catalytic properties, but it is also in great demand for ornamental purposes, is scarce and hence is very expensive. Platinum, for example, is used in both the cathode and anode of polymer electrolyte fuel cells (PEFC), which are considered to be efficient environmentally friendly power generators for the future. It is well-known that one of the main hindrances to the mass utilization of PEFCs is the price of platinum.

Because of its vast number of applications, many studies have been made on how to reduce the amount of platinum in catalysts. Methods include dispersing platinum nanoparticles in

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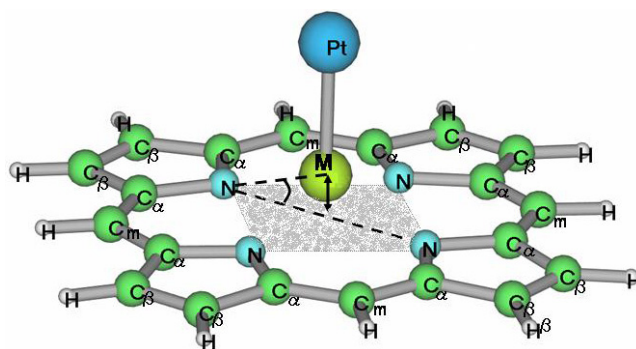


Figure 1. Geometry of MPor–Pt where M is Ge, Sn or Pt. The N plane (the mean plane formed by the four Ns of porphyrin) is shown as a shaded surface, the M–N plane distance as a double-headed arrow, and the angle between the M and the N planes as dashed lines.

porous silica, alumina and zeolites. But these materials that stably support Pt are not electrically conductive and therefore not suitable for electrocatalytic applications such as fuel cells. On the other hand, electrically conductive carbon-based support materials permit Pt nanoparticles to migrate and form larger clusters, leading to reduced catalytic activity over time [1, 2].

To overcome this problem, we suggested depositing individual platinum atoms on the surface of tin porphyrin [3]. Our calculations show that Pt can bond strongly on SnPor. Dispersing platinum atoms on a porphyrin surface will not only lower quantities of the precious metal needed to make catalytic surfaces but also—we believe—enhance their performance. The reasons for our belief are as follows: the top platinum metal (as shown in figure 1) has minimal steric hindrance for incoming molecules compared to metals in surfaces or porphyrins; the presence of a porphyrin chromophore can trap light energy, possibly assisting catalytic processes; and the perturbation on the electronic structure of Pt by SnPor, as our calculations indicate [3], enhances its catalytic properties.

Experimental studies have shown that both germanium (II) porphyrin (GePor) and tin (II) porphyrin (SnPor) can deposit metals—such as iron (Fe), magnesium (Mg), rhenium (Re) and cobalt (Co)—on its surface. The Mg and Co deposited on SnPor can further bond with metals such as mercury (Hg), manganese (Mn), cadmium (Cd), cobalt (Co) and zinc (Zn) forming a wire. Many of these compounds have been studied for their spectral, magnetic and electrochemical properties. Their structures have been confirmed by x-ray diffraction [4–9]. However, the deposition of platinum on germanium, tin or lead porphyrins has not been reported.

Since experimental studies have shown that GePor can also deposit metals, we have continued our search for means to reduce the platinum load on catalyst surfaces by comparing the interaction of Pt with all group 4A metal porphyrins, i.e. GePor, SnPor and PbPor. We aim to provide readers with a fundamental understanding of the resulting products (GePor–Pt, SnPor–Pt and PbPor–Pt). The direction of our present dynamics calculations on the catalysis of oxygen reduction on MPor–Pt was determined based on the results of this study.

2. Calculations

In our previous paper [3] we made calculations for the ground state of SnPor and compared our results with the geometry obtained experimentally by x-ray diffraction [10] to confirm the suitability of our chosen basis set and exchange–correlation functional, which were LanL2DZ

Table 1. Calculated geometric parameters of MPor–Pt (M = Ge, Sn, Pt).

| | GePor–Pt | SnPor–Pt [3] | PbPor–Pt |
|-----------------------------|----------|--------------|----------|
| Distance (Å) | | | |
| N plane–M | 0.679 | 0.823 | 0.947 |
| N–M | 2.113 | 2.205 | 2.278 |
| M–Pt | 2.283 | 2.418 | 2.472 |
| N–C $_{\alpha}$ | 1.399 | 1.396 | 1.393 |
| C $_{\alpha}$ –C $_{\beta}$ | 1.447 | 1.451 | 1.455 |
| C $_{\alpha}$ –C $_{m}$ | 1.390 | 1.398 | 1.403 |
| Angle (deg) | | | |
| M–N plane | 18.74 | 21.92 | 24.56 |

and B3LYP respectively. Our results were well within the expected accuracy of density functional calculations. Our calculations indicate that the ground state is a singlet, which is consistent with its observed diamagnetism. We also calculated the interaction between SnPor and Pt, and the properties of SnPor–Pt.

Following our previous study, we now show the results of our calculations for GePor–Pt and PbPor–Pt in comparison with SnPor–Pt. Likewise, we perform density functional calculations with Gaussian03 [11] using the LanL2DZ basis set and the B3LYP exchange–correlation functional. For C, H and N, LanL2DZ employs the Dunning–Huzinaga valence double-zeta (D95V) basis set [12]; for Sn and Pt, double-zeta basis sets for valence electrons were used with Los Alamos effective core potentials [13] due to the high atomic numbers of these two atoms.

We confirmed that the ground states of these compounds were singlets. We fully relaxed the geometries of all compounds.

3. Results and discussion

Our calculations gave energies of 3.13 eV for the binding of Pt on GePor and on SnPor, but only 1.99 eV for PbPor. This is consistent with the fact that metals (e.g. Fe) that bind weakly on GePor and SnPor have not been shown to bind on PbPor experimentally.

The relaxed geometries of MPor–Pt (M = Ge, Sn or Pb) are summarized in table 1. The geometric parameters are as shown in figure 1. The N plane (the mean plane formed by the four Ns of porphyrin) is shown as a shaded surface; the M–N plane distance is shown as a double-headed arrow; the angle between M and the N plane is shown as dashed lines. The bond distances between M and the N plane are accounted for by differences in the atomic radii of the metals (Ge = 1.52 Å, Sn = 1.72 Å, Pb = 1.81 Å). The trend in M–Pt bond distance can likewise be explained by differences in the atomic radii of M. As expected, the geometries of the porphyrin rings are not significantly different between the three types of MPor–Pt.

Table 2 shows the Mulliken charge distributions of GePor–Pt, SnPor–Pt and PbPor–Pt. A similar behaviour was observed for all MPor–Pt. This is understandable as Ge, Sn and Pb have very similar electronic configurations. The partial charges on M can be attributed primarily to their ionization potential (Ge (7.899 V), Sn (7.344 V) and Pb (7.416 V)). Germanium, having the highest ionization potential, carries the lowest partial positive charge. The Pt in all cases have partial negative charges (–0.53, –0.62, –0.50) indicating that these MPor have electron-donating tendencies.

The near HOMO and near LUMO states are shown in figures 2 and 3. We see here that the frontier orbitals are quite similar for all the Mpor–Pt. Valence Pt d-orbital characteristics

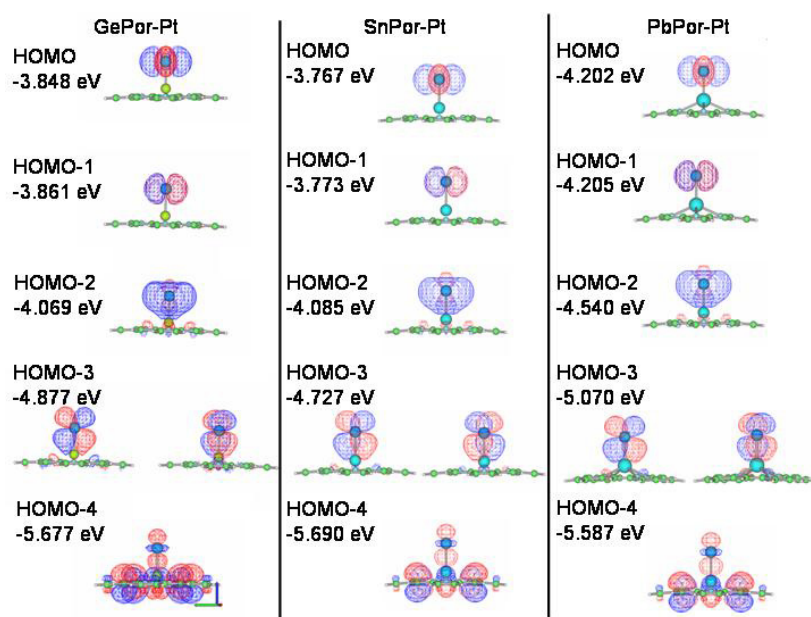


Figure 2. HOMO and near-HOMO levels of MPor–Pt.

Table 2. Mulliken charge distributions of MPor–Pt (M = Ge, Sn, Pt).

| | GePor–Pt | SnPor–Pt [3] | PbPor–Pt |
|--------------|----------|--------------|----------|
| Pt | −0.53 | −0.62 | −0.50 |
| M | 1.22 | 1.41 | 1.28 |
| N | −0.51 | −0.55 | −0.49 |
| C_{α} | 0.44 | 0.44 | 0.41 |
| C_{β} | −0.37 | −0.36 | −0.36 |
| C_m | −0.55 | −0.54 | −0.54 |

dominate HOMO and HOMO-1. This implies that MPor–Pt will have the same chemical properties as platinum atoms or clusters in cases where the reaction involves the HOMO and HOMO-1 (i.e. electron donation to vacant orbitals of adsorbates).

The vacant LUMO levels are characterized by p_z -orbital contributions from carbon and nitrogen of the porphyrin ring and some d-orbital contribution from Pt. Consequently, we cannot conclusively predict that MPor–Pt will have the same chemical properties as platinum atoms or clusters for cases where the reaction involves the LUMO (i.e. electron reception from the filled orbitals of adsorbates). It is also observed that, above the LUMO, the orders of vacant orbitals vary for each MPor–Pt. This is primarily due to differences in energies of molecular orbitals that involve M, which are LUMO + 1 and LUMO + 4 for GePor–Pt, LUMO + 2 and LUMO + 3 for SnPor–Pt, and LUMO + 1 and LUMO + 3 for PbPor–Pt.

We searched for the bonding orbitals between MPor and Pt. The results are shown in figure 4. In each case, the Pt d_{z^2} orbital binds with the sp_z orbital of M. This suggests that the bond between Pt and M is more of a metal–ligand interaction than a metal–metal bond. In the case of Sn–Por and Pb–Por, we also see interaction between the p_z orbitals of N from the porphyrin and the d_{z^2} orbital of platinum. (This overlap is not found in PbPor–Pt due to the large atomic radius of Pb, which puts Pt in a position too far away to interact with the

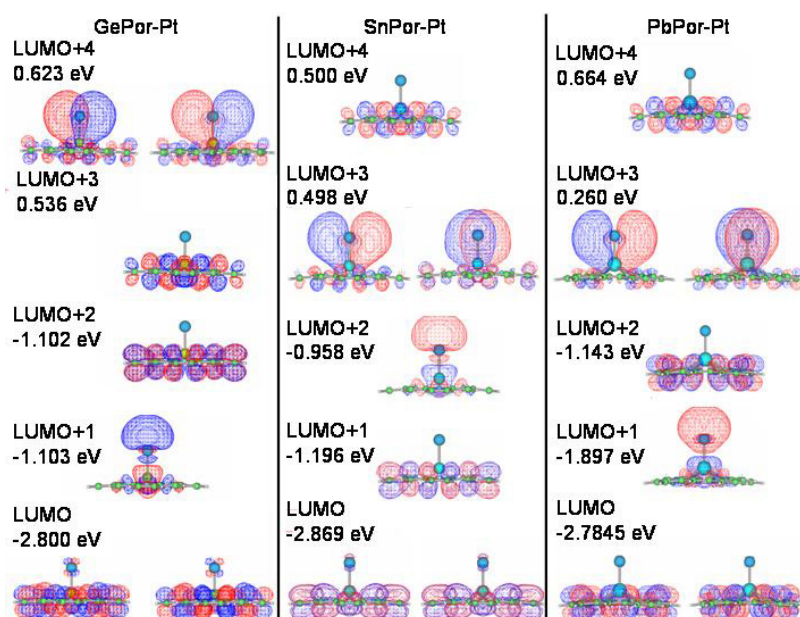


Figure 3. LUMO and near-LUMO levels of MPor-Pt.

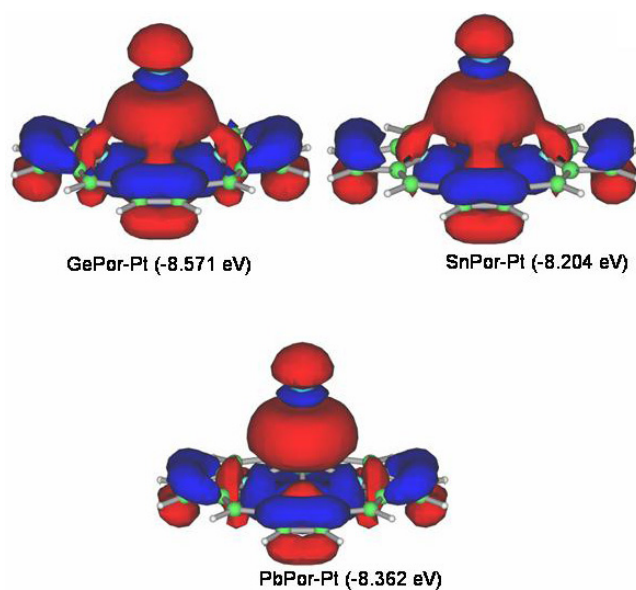


Figure 4. Bonding orbitals of MPor-Pt.

porphyrin.) More importantly, upon comparing the energies of orbitals in figures 2–4, it can be seen that the bonding orbitals (figure 4) are much lower in energy than the frontier orbitals. This indicates that electrons in these bonding states will not be involved in chemical reactions that will result in the breaking of the Pt–MPor bond, implying that Pt will deposit tightly on MPor during chemical reactions.

4. Conclusion

In conclusion, we showed the geometric and electronic structures of GePor–Pt, SnPor–Pt and PbPor–Pt.

We also showed that platinum can bond strongly on both GePor and SnPor with a binding energy of 3.13 eV. On the other hand, the binding of Pt on Pb–Por is weaker by about 1 eV. Also, the electrons in the Pt–MPor bonding orbitals are much lower than their corresponding HOMOs and LUMOs, indicating that electrons in these bonding states will not be involved in chemical reactions that will result in the breaking of the Pt–MPor bond. From the above discussion, we conclude that Pt will deposit stably on SnPor and GePor.

Most importantly, we show that valence Pt d-orbital characteristics dominate the HOMO and HOMO-1 of MPor–Pt. This implies that MPor–Pt will have the same chemical properties as platinum atoms or clusters in cases where the reaction mainly involves the HOMO and/or HOMO-1 (i.e. electron donation to vacant orbitals of adsorbates), of which the oxygen reduction reaction in fuel cells is an example. This argument is further reinforced by the fact that Pt atoms in MPor–Pt have partial negative charges.

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