

P-Block Elements Activate Pt Surfaces for the Electrooxidation of Alcohols and Polyols When Promoting the –OH formation

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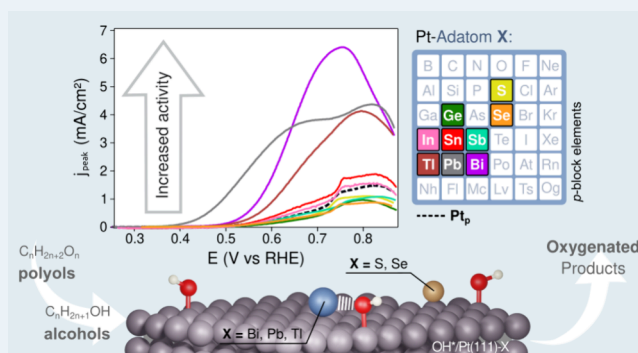
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ABSTRACT: The electro-oxidation of alcohols and polyols plays a pivotal role in energy conversion and biomass utilization, offering profound implications for producing energy via fuel cells and the synthesis of value-added chemicals, including biomass derivatives and green hydrogen, through electrolyzers. Addressing the challenge of catalyst poisoning and the need for enhanced catalytic activity, this study delves into utilizing p-block elements (Bi, Pb, Tl, Se, Ge, Sb, Sn, In, and S) adsorbed on platinum electrodes. This approach is chosen to mitigate the drawbacks associated with Pt or Pd, including poisoning by CO and other strongly adsorbed unknown intermediates, and to provide information toward developing more suitable catalysts for the task at hand. Through a combination of electrochemistry, analytical chemistry techniques, and density functional theory (DFT) calculations, we demonstrate that these adatoms significantly increase the activity of Pt electrodes by stabilizing hydroxyl (–OH) species rather than altering the stability of carbon-adsorbed alcohol intermediates. This stabilization of –OH species is identified as the rate-determining step in the electro-oxidation process, suggesting a general trend that could apply to the oxidation of a wide range of alcohols and polyols. Our findings not only shed light on the mechanistic aspects of alcohol and polyol electro-oxidation but also highlight how this knowledge paves the way for the rational design of materials, in this specific case, catalysts for energy conversion and biomass utilization applications.

KEYWORDS: p-block elements, platinum electrodes, hydroxyl species stabilization, alcohols and polyols, density functional theory (DFT)



INTRODUCTION

The electro-oxidation of alcohols and polyols holds considerable importance in various domains, primarily in the realms of energy conversion and biomass utilization. In fuel cells, these compounds are used as fuel sources from which chemical energy is converted into electrical energy, whereas in electrolyzers, they facilitate water oxidation by reducing the operating potential needed to generate green hydrogen.^{1,2}

The catalysts used are categorized primarily by the presence or absence of platinum-group metals, from which Pt and Pd show the highest activity and are the most commonly used active elements in catalyst development. In particular, platinum is considered the most active likely due to having the lowest d-band center.³ The caveat about these elements is that they are both prone to poisoning by CO adsorption and other less-known intermediates, which occurs across all pH ranges.^{4,5} At this point, it is worth noticing that the identity of these intermediates has not been convincingly confirmed by any spectroscopic technique and most of the mechanistic details for the reaction have been proposed through computational experiments.^{6,7} This limitation can be circumvented by synthesizing catalyst nanoparticles alloyed with different

elements, such as Ni⁸ and elements from the p-block,⁹ as well as by tuning the catalyst structure and/or employing an active support phase.^{10,11} In particular, p-block elements can be used to modify the surface of Pt electrodes through adsorption (and henceforth referred to as adatoms) and show multiple effects when used to oxidize glycerol from preventing CO adsorption to changing both the reaction activity and selectivity.^{9,12}

Pt and Pd catalysts modified by p-block elements have been used to oxidize polyols in heterogeneous catalysis, and it has been shown that their modification by Bi or Pb changes the reaction selectivity, favoring the oxidation of secondary hydroxyls.^{13,14} Similar results were obtained with Pt–Bi and Pt–Pb catalysts for the electro-oxidation of polyols in acidic media,^{9,12,15} and it was proposed that a similar oxidation

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mechanism to that of heterogeneous catalysis was followed.^{12,16} However, it was later clarified that the change in selectivity was due to the openness of the catalyst surface and its consequences in the intermediates' stability.¹⁷ In alkaline media, whereas the reaction selectivity remained unchanged, a notable enhancement in catalyst activity was observed. This suggests that alkaline electrolytes possess a heightened potential to significantly improve the efficiency of green hydrogen production.^{18,19}

The majority of studies concerning the oxidation of polyols are focused on acidic media, with many propositions aiming to elucidate the reaction mechanism on these Pt-adatom surfaces. Of particular interest is a study on formic acid oxidation on Pt catalysts modified by p-block elements²⁰ in which the authors showed that the adatoms retain a partial charge when adsorbed and that the positively charged ones improve the reaction activity. In other words, they showed that activity enhanced with increasing electronegativity difference between Pt and that of the p-block elements.

Despite these insights, the influence of adatoms on the electro-oxidation of alcohols and polyols in alkaline media has remained largely unexplored, particularly from a microscopic perspective, leaving a gap in our understanding of the underlying mechanisms at play. This study undertakes a systematic examination to uncover how p-block elements adsorbed on Pt electrodes impact the activity toward glycerol electro-oxidation in alkaline conditions. Through the density functional theory (DFT), we demonstrate that adatoms significantly influence the stability of $-OH$ species compared to C-adsorbed glycerol intermediates. The adatoms that enhance Pt activity for glycerol electro-oxidation are those that stabilize the $-OH$ species, indicating that the formation of this intermediate is the rate-determining step of the reaction and that the adatoms provide the active sites for the generation of reactive OH species, promoting a bifunctional mechanism. Extending our findings to other alcohols and polyols, namely, ethanol, ethylene glycol, and erythritol, we observed consistent results, underscoring the pivotal role of $-OH$ stabilization on Pt electrodes in promoting the electro-oxidation of a broad spectrum of molecules.

EXPERIMENTAL SECTION

Electrochemical System and Surface Preparation. All measurements were performed at room temperature in a standard three-electrode cell controlled by a PGSTAT 204 potentiostat from Autolab. The working electrode (WE) was a polycrystalline platinum (Pt_p) wire with a spherical end, whereas the counter electrode (CE) was a platinum foil, both cleaned by immersion in aqua regia for 30s, rinsed with ultrapure water, flame-annealed in a butane flame, and then quenched with ultrapure water. The reference electrode was a reversible hydrogen electrode (RHE), and all potentials reported here are referred to it.

Before each measurement, a voltammogram of a clean Pt_p surface in 0.5 M H_2SO_4 was obtained, and after, the electrode was rinsed with ultrapure water and transferred to the electrochemical cell containing the NaOH + glycerol solution. The electrode was submerged into the solution while polarized at 0.20 V, and then the potential cycling began. Modification of the Pt_p electrode by p-block elements was carried out within the glycerol-containing cell by adding a small (<50 μL) amount of a dilute solution containing a salt of the element

(for further details, refer to Figure S2 of the Supporting Information).

Chemicals. Solutions were made using ultrapure water (18.2 M Ω /cm, 25 °C, Millipore), and all chemicals were used without prior filtration. The chemicals used were sulfuric acid (ISO grade, Merck Emsure), nitric acid (p.a. ACS, LS Chemicals), hydrochloric acid (p.a. ACS, Vetec Chemistry), sodium hydroxide (semiconductor grade, 99.99% trace metal basis, Sigma-Aldrich), glycerol (ACS grade, Sigma-Aldrich), lead(II) nitrate (99.999% trace metal basis, Sigma-Aldrich), bismuth(III) oxide (ReagentPlus, Sigma-Aldrich), thallium(I) sulfate (99.99% trace metal basis, Sigma-Aldrich), antimony oxide (99.999% trace metal basis, Sigma-Aldrich), indium(III) nitrate hydrate (99.99% trace metal basis, Sigma-Aldrich), tin(II) sulfate ($\geq 95.0\%$, Sigma-Aldrich), germanium(IV) oxide (99.999% trace metal basis, Sigma-Aldrich), selenium(IV) oxide (99.9% trace metal basis, Sigma-Aldrich), sodium sulfide nonahydrate (p.a. ACS, Vetec), ethanol (EMSURE ACS, ISO, Reag. Ph Eur, Supelco), ethylene glycol (Reagent Plus, $\geq 99\%$, Sigma-Aldrich), and *meso*-erythritol ($\geq 99\%$, Sigma-Aldrich).

Computational Experiments. The DFT simulations were performed with the Vienna Ab Initio Simulation Package (VASP)^{21,22} using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange–correlation functional.^{23,24} For the inclusion of dispersion effects, the Grimme-D3 corrections were taken into account. The projector augmented wave (PAW)²⁵ method was employed to account for the core electron contributions, and a cutoff energy of 450 eV was used for the plane-wave basis in all calculated systems.

In our last study,¹⁵ several structures were explored for different glycerol and erythritol double-dehydrogenated intermediates on Pt(111), Pt(111)-Bi, and Pt(111)-Bi₂O₃ surfaces, making it possible to find the most favorable ones. These intermediates (or adsorption systems), composed of a Pt surface and an adsorbing polyol derivative, are referred to as “key intermediaries” as their relative stability can reveal information about the reaction selectivity. In this present study, new adatoms (S, Se, Tl, and Pb) were explored to understand the activity trend obtained with the Pt-adatom electrodes. It is worth noticing that, in this work, we are not focusing on selectivity insights, as several complex reactions occur in the alkaline medium solution, making it challenging to distinguish which are products generated through electrochemical or chemical reactions.^{26–28}

A Pt(111) surface was modeled using a $p(4 \times 4)$ slab with five platinum layers and 20 Å of vacuum along the direction normal to the surface. The modeling was based on a calculated cell parameter of 3.967 Å (1.2% different from the literature value). The two bottom layers were kept fixed during the calculations to simulate the Pt bulk. For the adatom surfaces, a single atom was placed in an f.c.c. site ($\Theta = 1/16$ ML) following previous stability calculations for Bi adatom modification.

We choose the most stable structures of the double-dehydrogenated intermediates (identified as intermediates 1,1-G; 1,2-G; and 1,3-G) previously found for Pt(111)-Bi as initial geometry for all new adatom systems; i.e., bismuth was replaced with the atom of interest, and the system was relaxed. This process was done for all four new elements: S, Se, Tl, and Pb (Figure 1). The glycerol and H₂ molecules, involved in the reaction, were also modeled in an asymmetric box of 20 × 21 × 19 Å³. Therefore, the choice of these three intermediates is

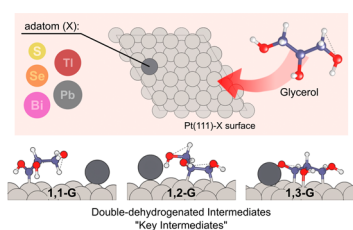
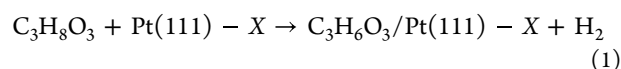


Figure 1. Explored glycerol intermediates and adatoms. The nomenclature of the intermediates follows which glycerol carbons undergo dehydrogenation and are bonded to the surface; for example, 1,3-G refers to dehydrogenation occurring at carbons 1 and 3.

connected to our previous contributions. We believe that this is a reasonable selection, less arbitrary than using just one intermediate and significantly less time-consuming than exploring every possible intermediate for each surface, which would be beyond our capabilities.

Convergence criteria of 10^{-6} eV and 0.01 eV/Å were used for the energy and the forces, respectively. The Brillouin zone was sampled using the Monkhorst–Pack method with a $3 \times 3 \times 1$ k -point mesh for the free surfaces, and for the intermediates, for the free molecules' calculations, only the gamma point was used. Vibrational frequencies were obtained for thermodynamic corrections of all adsorption systems and molecules. In addition, static calculations were performed to gain a better understanding of the electronic structures through analyses such as Bader charge and charge density differences.

The stability trend was obtained by calculating the adsorption free energies of the different explored systems, following the formation reaction of the intermediates:



where X is the adatom, and the first term of the products, $\text{C}_3\text{H}_6\text{O}_3/\text{Pt}(111)-\text{X}$, is the intermediate or adsorption system. Note that the same equation was used for the adsorption systems containing the Pt(111) free surface. The adsorption energy can be estimated according to eq 2, where E is the DFT energy of the component.

$$\Delta E_{\text{ads}} = E_{\text{C}_3\text{H}_6\text{O}_3/\text{Pt}(111)-\text{X}} + E_{\text{H}_2} - E_{\text{C}_3\text{H}_8\text{O}_3} - E_{\text{Pt}(111)-\text{X}} \quad (2)$$

Finally, the adsorption free energy, as a function of the DFT energy (E) and thermodynamic contributions, including zero point energy (ZPE), thermal (U), and entropic corrections (S), can be obtained (eq 3).

$$\Delta G_{\text{ads}} = \Delta E_{\text{ads}} + \Delta \text{ZPE}_{\text{ads}} + \Delta U_{\text{ads}} - T \times \Delta S_{\text{ads}} \quad (3)$$

ELECTROCHEMICAL RESULTS AND DISCUSSION

We have investigated a total of nine different Pt-adatom systems and the summary of the electrochemical results is shown in Figure 2, whereas the complete results are provided in Figure S1. In these experiments, we have chosen to directly add the p-block adatoms to the electrolyte containing glycerol so that adatom deposition and oxidation took place on the same cell. This approach is different from that originally proposed by Clavilier et al.,²⁹ where the adatom is deposited outside of the electrochemical cell, without potential control. As showed in our previous publications,^{18,19} we followed this approach because it provides both a higher anodic current and also a more stable electrode response, where the peak current

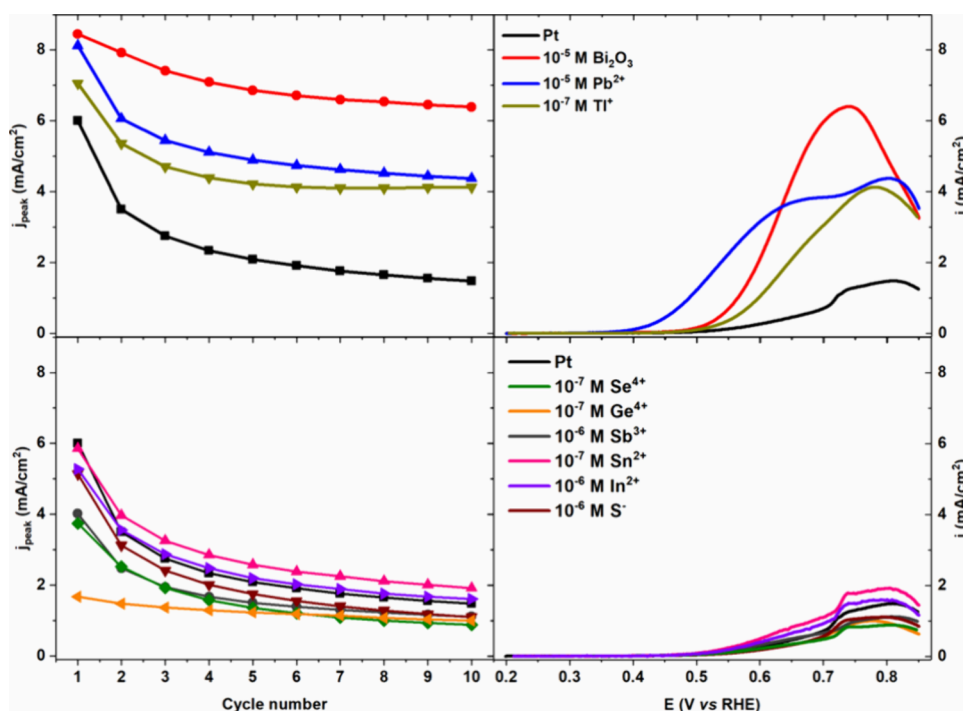


Figure 2. Right: Evolution of peak current density (j_{peak}) with cycle number for each Pt-adatom system, with each element at their optimal concentration (i.e., the concentration in which the highest increase in anodic current is observed, as well as where j_{peak} decreases more slowly during continuous cycling) in solution. Left: Positive-going sweep of the 10th scan during cyclic voltammetry in 0.1 M NaOH + 0.1 M glycerol electrolyte, with addition of each p-block element as specified in the graph subtitles, using a polycrystalline Pt electrode with a 10 mV/s sweep rate. Data for the Pt–Pb and Pt–Bi systems have been taken from refs 18 and 19

density (j_{peak}) decreases more slowly with adatoms in solution (see Figure S2 and refs 18 and 19). Therefore, in these works, we have not controlled the adatom coverage as is usually done in this field, but used the optimal ion concentration to maximize the surface activity.

Our results show that of all elements examined, only three—lead, bismuth and thallium—provided a significant improvement to the activity of the Pt_p electrode. For all ions, we observe a similar trend, i.e., activity increases with ionic concentration up to a certain point, after which the electrode activity begins to decrease (cf. Figure S1), with the only exception being the Pt–Ge system, where Pt is heavily deactivated by concentrations as low as 10^{−7} M Ge⁴⁺ in solution. All three Pt-adatom systems were studied using FTIR and HPLC (see refs 18 and 19 for Pt–Bi and Pt–Pb, respectively, and Figures S3 and S4 for Pt–Tl). In all cases, we observe the absence of CO adsorption after deposition of the adatoms as well as a decrease in carbonate formation (resulting from the total oxidation of glycerol). It is well-known that the formation of CO is a site-demanding reaction; then, the poisoning inhibition by adding adatoms to a Pt surface is expected. However, in this scenario, it is clear that the promotion of the catalysis is not only connected with this third-body effect, but there is a clear activation of the reaction by Bi, Pb, and Tl as they increase the observed currents and promote the reaction at more negative electrochemical potentials. We will revisit this relevant point in the Computational Results and Discussion section.

As mentioned in the introduction, there is one similar study to this one but for the electro-oxidation of formic acid.^{20,30} However, unlike that article, our results cannot be explained simply by considering the difference in electronegativity of the elements (Table S1). Besides, the difference in electronegativity is an indirect descriptor, not giving a microscopic insight into the physicochemical phenomena behind these observations. Thus, to understand our electrochemical results, we employed DFT calculations to understand how some reaction intermediates (Figure 1 and refs 15 and 17) are affected by the p-block adatoms.

COMPUTATIONAL RESULTS AND DISCUSSION

We began by investigating how different adatoms affect the stability of some glycerol-derived intermediates (Figure 1). The adsorption free energies for Pt(111), Pt(111)-S, Pt(111)-Se, Pt(111)-Bi, Pt(111)-Tl, and Pt(111)-Pb were calculated and are presented in Figure 3, whereas Figure 4 shows the structures of the adsorption systems for all five adatoms.

In Figure 3, we observe similar energy trends for all modeled surfaces, where intermediate 1,1-G is the least favorable and the other two intermediates are the most stable ones. In general, and in line with the electrochemical results, we can separate the results into two groups: Bi, Tl, and Pb at more negative energies and S and Se showing very similar results and at more positive energies than Pt.

However, as we noted previously,^{15,17} the differences in the free adsorption energies of the intermediates are rather small, lower, or close to the well-established experimental uncertainty of the technique (≈ 0.2 eV). On the other hand, the effect of the adatoms in the electrode activity is noticeable, reaching different orders of magnitude at some electrochemical potentials. Therefore, these results suggest that the stability of the glycerol derivatives is not the key to understanding our electrochemical results.

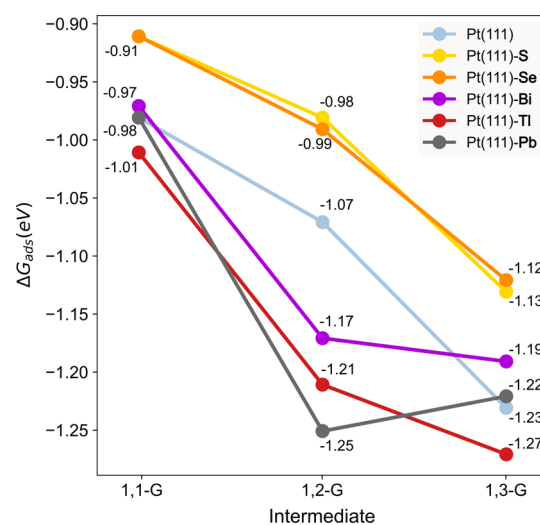


Figure 3. Adsorption free energy trend for the glycerol derivatives on Pt(111) and on Pt surfaces with different adatoms (S, Se, Bi, Pb, and Tl).

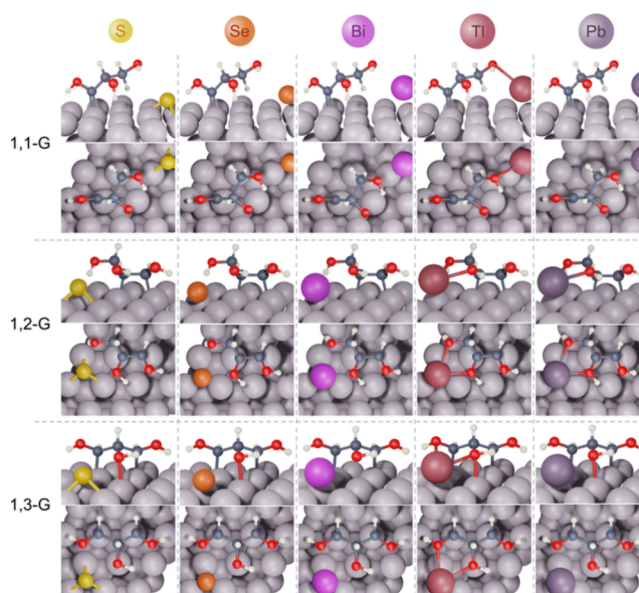
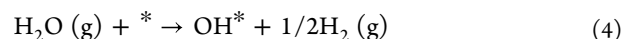


Figure 4. Structures of intermediates 1, 2, and 3, arranged in the rows of the table, for all Pt(111)-X surfaces, with X being S, Se, Bi, Tl, or Pb adatoms (columns).

Since oxygenated species are obtained as products with all adatoms (Figure S4 and previous reports^{9,18,19}), the reaction likely involves oxygenated intermediates, such as the hydroxyl radical. This proposition was made in other studies^{31–33} on electro-oxidation reactions. Therefore, to complement the activity discussion, DFT calculations were also performed for the hydroxyl intermediate on six different surfaces. These calculations are shown in Figure 5, where we examine how the ΔG_{ads} for the adsorbed hydroxyl species changes in the presence of the adatoms. Similar to the glycerol intermediates described in the methodology section, the ΔG_{ads} values were obtained with thermodynamic corrections. The ΔE_{ads} term corresponds to the reaction:



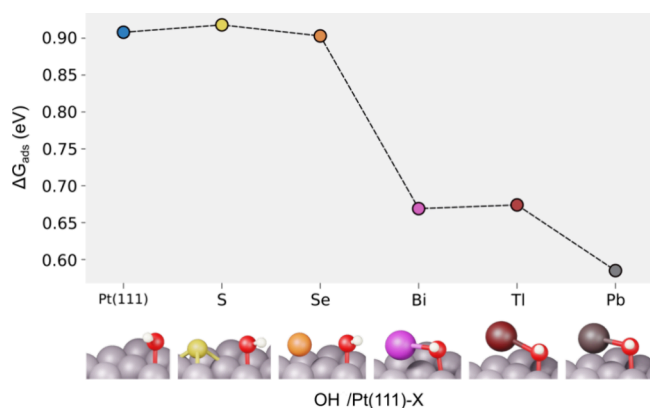


Figure 5. Structure of the intermediate HO_{ads} for all Pt(111)-X surfaces, with X being S, Se, Bi, Tl, or Pb adatoms, and their respective adsorption free energies. For additional details on solvation effects, comparisons with experimental and theoretical data, and distances between atoms, refer to the [Supporting Information](#).

Which involves both the dissociation of water and the adsorption of the hydroxyl (eq 5):

$$\Delta E_{\text{ads}} = E_{\text{OH/Pt(111)-X}} + 1/2E_{\text{H}_2} - E_{\text{H}_2\text{O}} - E_{\text{Pt(111)-X}} \quad (5)$$

The results can be divided into two groups: the first containing Pt(111), Pt(111)-S, and Pt(111)-Se surfaces with higher adsorption free energy values and the second including Pt(111)-Bi, Pt(111)-Tl, and Pt(111)-Pb with lower adsorption energies. Contrary to what was observed for glycerol derivatives, the difference between these groups is significant, showing that the hydroxyl intermediate is more favorable in the presence of Bi, Tl, or Pb, i.e., the adatoms that increase the electroactivity of Pt. We also performed the same calculations but using implicit solvation, confirming the previously discussed trend (see the [Supporting Information](#)).

If the reaction is accelerated because of the promotion of adsorbed $-\text{OH}$ species rather than changes in the relative stability of the organic molecule derivatives, then it is reasonable to believe that we should get similar results with other alcohols or polyols. Therefore, we performed electrochemical experiments with ethanol, ethylene glycol (a two-carbon polyol), and erythritol (a four-carbon polyol) (see [Figure 6](#)). We again observe that while the presence of Se does not affect the Pt activity, the adsorption of Pb activates the surface, suggesting that this dependency on the availability of adsorbed oxygenated species is a general trend for the electro-oxidation of all alcohols and polyols in alkaline medium.

To shed more light on the generation of $-(\text{OH})_x$ species, we cycled the Pt-X electrodes in the absence of glycerol ([Figure S5](#)) and observed that electrode oxidation begins earlier when Bi, Tl, and Pb are present on the electrode surface. This oxidation current might be due to the oxidation of water to form superficial $\text{PtO}_x/\text{Pt}-(\text{OH})_x$ species or the oxidation of the adatom. It is worth noting that both events would contribute to increasing the OH coverage, agreeing with the DFT calculations. In the former case, OH is generated while the oxidized adatom will attract and bond to the highly available OH^- species from the alkaline solution. Another related observation is that even in the presence of the most favorable adatoms, the alcohol oxidation currents begin to increase at much higher potentials (the so-called onset potentials) than what one would expect from thermodynamics

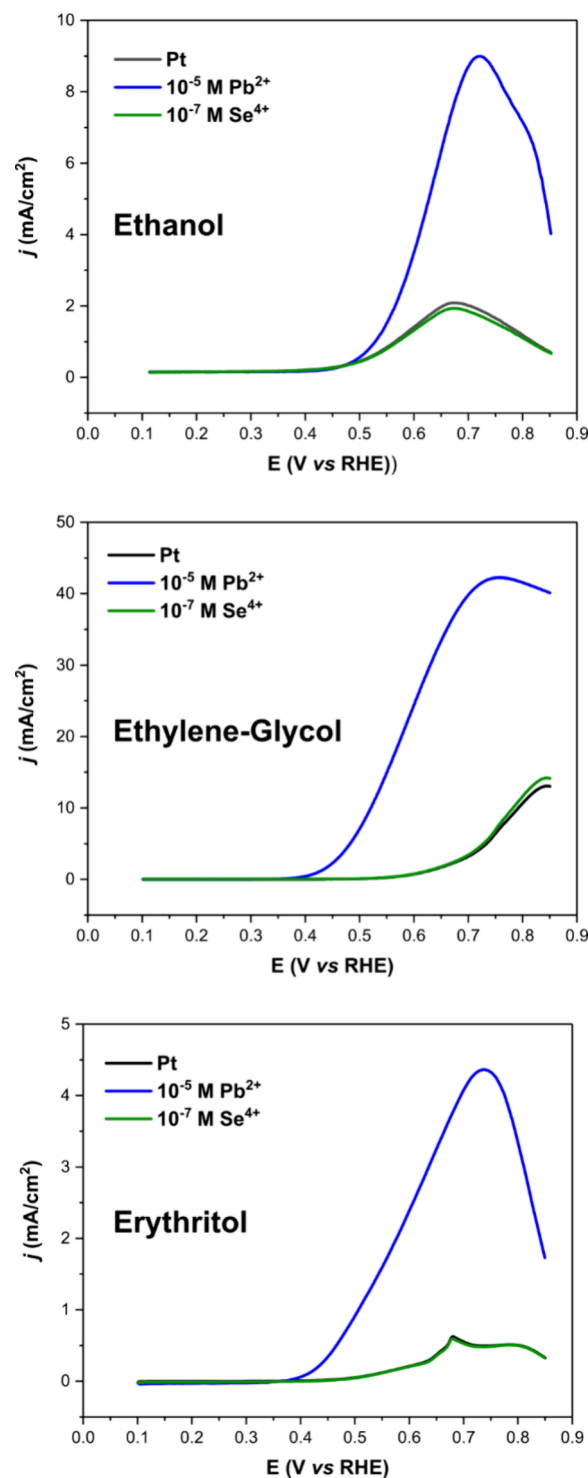


Figure 6. Positive-going sweep of the 10th scan during cyclic voltammetry in 0.1 M NaOH + 0.1 M ethanol (top), 0.1 M ethylene glycol (mid), and 5 mM erythritol (bottom) electrolyte, with addition of a p-block element as specified in the graph subtitles, using a polycrystalline Pt electrode with a 10 mV/s sweep rate.

(around 0 V vs RHE),³⁴ which is understandable given the complexity of the reaction. In this context, the DFT and electrochemistry results in the presence and absence of the alcohols/polyols strongly suggest that $-(\text{OH})_x$ species are necessary to oxidize the organic molecule and serve as a threshold for the reaction.

After highlighting the importance of the OH species, we return to DFT to end with a deeper discussion about the reaction mechanism. Table S3 presents the distances between the O atoms with the Pt atoms and the adatoms. The results agree with the image shown in Figure 5; i.e., the OH species are mainly interacting with the Pt surface for the surfaces containing the negatively charged adatoms (S and Se). In the presence of Bi, Tl, and Pb, the stabilized structure changes radically, slightly increasing the O–Pt distance and drastically decreasing the O–X distance, indicating a strong interaction of the OH species with these adatoms. Therefore, our calculation suggests that the adatoms provide the active sites for the formation of active OH species, which will then react with the adsorbed glycerol derivative intermediates on the Pt surface to produce the previously mentioned oxygenated products. In other words, we hypothesize that the adatoms promote a bifunctional mechanism.

CONCLUSIONS

This investigation elucidates the significant impact of p-block element adatoms on the electro-oxidation of glycerol on Pt electrodes in alkaline media, marking a pivotal advancement in the understanding of catalytic processes for energy conversion and biomass utilization. The key findings reveal that the presence of these adatoms enhances the electrochemical activity of Pt electrodes predominantly through the stabilization of adsorbed hydroxyl species rather than by modifying the stability of carbon-adsorbed glycerol intermediates. This mechanistic insight, supported by both experimental and theoretical analyses, underscores the rate-determining role of –OH species stabilization in the electro-oxidation process, suggesting the promotion of a bifunctional mechanism.

Furthermore, the observed trend suggests the broader applicability of this approach to the oxidation of various alcohols and polyols, indicating a potential universal strategy for improving catalytic efficiency in energy-related applications. The integration of electrochemistry, analytical chemistry techniques, and DFT calculations has provided a comprehensive understanding of the interactions at play, offering a solid foundation for future catalyst design and optimization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c02443>.

Complete set of electrochemical results obtained with all the adatoms; in situ FTIR and online HPLC results obtained with the system Pt–Tl; solvation effects; and computational comparison of hydroxyl radical adsorption with literature (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Holade, Y.; Tuleushova, N.; Tingry, S.; Servat, K.; Napporn, T. W.; Guesmi, H.; Cornu, D.; Kokoh, K. B. Recent Advances in the Electrooxidation of Biomass-Based Organic Molecules for Energy, Chemicals and Hydrogen Production. *Catal. Sci. Technol.* **2020**, *10* (10), 3071–3112.
- (2) Dodekatos, G.; Schünemann, S.; Tüysüz, H. Recent Advances in Thermo-, Photo-, and Electrocatalytic Glycerol Oxidation. *ACS Catal.* **2018**, *8* (7), 6301–6333.
- (3) Li, T.; Harrington, D. A. An Overview of Glycerol Electro-oxidation Mechanisms on Pt, Pd and Au. *ChemSusChem* **2021**, *14* (6), 1472–1495.
- (4) Simões, M.; Baranton, S.; Coutanceau, C. Electro-Oxidation of Glycerol at Pd Based Nano-Catalysts for an Application in Alkaline Fuel Cells for Chemicals and Energy Cogeneration. *Appl. Catal. B Environ.* **2010**, *93* (3–4), 354–362.
- (5) Simões, M.; Baranton, S.; Coutanceau, C. Enhancement of Catalytic Properties for Glycerol Electrooxidation on Pt and Pd Nanoparticles Induced by Bi Surface Modification. *Appl. Catal. B Environ.* **2011**, *110*, 40–49.
- (6) Liu, B.; Greeley, J. A Density Functional Theory Analysis of Trends in Glycerol Decomposition on Close-Packed Transition Metal Surfaces. *Phys. Chem. Chem. Phys.* **2013**, *15* (17), 6475–6485.
- (7) Liu, B.; Greeley, J. Decomposition Pathways of Glycerol via C-H, O-H, and C-C Bond Scission on Pt(111): A Density Functional Theory Study. *J. Phys. Chem. C* **2011**, *115* (40), 19702–19709.
- (8) Carvalho, L. L.; Colmati, F.; Tanaka, A. A. Nickel–Palladium Electrocatalysts for Methanol, Ethanol, and Glycerol Oxidation Reactions. *Int. J. Hydrogen Energy* **2017**, *42* (25), 16118–16126.
- (9) Kwon, Y.; Hersbach, T. J. P.; Koper, M. T. M. Electro-Oxidation of Glycerol on Platinum Modified by Adatoms: Activity and Selectivity Effects. *Top. Catal.* **2014**, *57* (14–16), 1272–1276.
- (10) Li, D. N.; Wang, A. J.; Wei, J.; Zhang, Q. L.; Feng, J. J. Dentritic Platinum–Palladium/Palladium Core-Shell Nanocrystals/Reduced Graphene Oxide: One-Pot Synthesis and Excellent Electrocatalytic Performances. *J. Colloid Interface Sci.* **2018**, *514*, 93–101.
- (11) Liu, M. T.; Chen, L. X.; Li, D. N.; Wang, A. J.; Zhang, Q. L.; Feng, J. J. One-Pot Controlled Synthesis of AuPd@Pd Core-Shell Nanocrystals with Enhanced Electrocatalytic Performances for Formic Acid Oxidation and Glycerol Oxidation. *J. Colloid Interface Sci.* **2017**, *508*, 551–558.
- (12) Kwon, Y.; Birdja, Y.; Spanos, I.; Rodriguez, P.; Koper, M. T. M. Highly Selective Electro-Oxidation of Glycerol to Dihydroxyacetone on Platinum in the Presence of Bismuth. *ACS Catal.* **2012**, *2* (5), 759–764.
- (13) Abbadì, A.; van Bekkum, H. Highly Selective Oxidation of Aldonic Acids to 2-Keto-Aldonic Acids over Pt-Bi and Pt-Pb Catalysts. *Appl. Catal. A, Gen.* **1995**, *124* (2), 409–417.
- (14) Wenkin, M.; Ruiz, P.; Delmon, B.; Devillers, M. The Role of Bismuth as Promoter in Pd-Bi Catalysts for the Selective Oxidation of Glucose to Gluconate. *J. Mol. Catal. A Chem.* **2002**, *180* (1–2), 141–159.
- (15) Soffiati, G.; Yukuhiro, V. Y.; Raju, S. P.; De Souza, M. B. C.; Marquezini, L.; da Silva, E. Z.; Fernández, P. S.; San-Miguel, M. A. Electro-Oxidation of Polyols on Bi-Modified Pt in Acidic Media (HClO₄). Understanding Activity and Selectivity Trends. *Chem-CatChem* **2023**, *15* (9), No. e202300252.
- (16) García, A. C.; Birdja, Y. Y.; Tremiliosi-Filho, G.; Koper, M. T. M. Glycerol Electro-Oxidation on Bismuth-Modified Platinum Single Crystals. *J. Catal.* **2017**, *346*, 117–124.
- (17) Soffiati, G.; Bott-Neto, J. L.; Yukuhiro, V. Y.; Pires, C. T. G. V. M. T.; Lima, C. C.; Zanata, C. R.; Birdja, Y. Y.; Koper, M. T. M.; San-Miguel, M. A.; Fernández, P. S. Electrooxidation of C 4 Polyols on Platinum Single-Crystals: A Computational and Electrochemical Study. *J. Phys. Chem. C* **2020**, *124* (27), 14745–14751.
- (18) de Souza, M. B. C.; Vicente, R. A.; Yukuhiro, V. Y.; V. M. T. Pires, C. T. G.; Cheuquepán, W.; Bott-Neto, J. L.; Solla-Gullón, J.; Fernández, P. S. Bi-Modified Pt Electrodes toward Glycerol Electrooxidation in Alkaline Solution: Effects on Activity and Selectivity. *ACS Catal.* **2019**, *9* (6), 5104–5110.
- (19) de Souza, M. B. C.; Yukuhiro, V. Y.; Vicente, R. A.; Vilela Menegaz Teixeira Pires, C. T. G.; Bott-Neto, J. L.; Fernández, P. S. Pb- and Bi-Modified Pt Electrodes toward Glycerol Electrooxidation in Alkaline Media. Activity, Selectivity, and the Importance of the Pt Atoms Arrangement. *ACS Catal.* **2020**, *10* (3), 2131–2137.
- (20) Ferre-Vilaplana, A.; Perales-Rondón, J. V.; Feliu, J. M.; Herrero, E. Understanding the Effect of the Adatoms in the Formic Acid Oxidation Mechanism on Pt(111) Electrodes. *ACS Catal.* **2015**, *5* (2), 645–654.
- (21) Vargas-Hernández, R. A. Bayesian Optimization for Calibrating and Selecting Hybrid-Density Functional Models. *J. Phys. Chem. A* **2020**, *124* (20), 4053–4061.
- (22) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561.
- (23) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B* **1993**, *48* (7), 4978–4978.
- (24) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (25) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59* (3), 1758–1775.
- (26) Kwon, Y.; Lai, S. C. S.; Rodriguez, P.; Koper, M. T. M. Electrocatalytic Oxidation of Alcohols on Gold in Alkaline Media: Base or Gold Catalysis? *J. Am. Chem. Soc.* **2011**, *133* (18), 6914–6917.
- (27) Hu, W.; Lowry, B.; Varma, A. Kinetic Study of Glycerol Oxidation Network over Pt-Bi/C Catalyst. *Appl. Catal. B Environ.* **2011**, *106* (1–2), 123–132.
- (28) Dai, C.; Sun, L.; Liao, H.; Khezri, B.; Webster, R. D.; Fisher, A. C.; Xu, Z. J. An Efficient One Pot Conversion of Glycerol to Lactic Acid Using Bimetallic Gold-Platinum Catalysts on a Nanocrystalline CeO₂ Support. *J. Catal.* **2017**, *356*, 14–21.
- (29) Clavilier, J.; Feliu, J. M.; Aldaz, A. An Irreversible Structure Sensitive Adsorption Step in Bismuth Underpotential Deposition at Platinum Electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *243* (2), 419–433.
- (30) Perales-Rondón, J. V.; Ferre-Vilaplana, A.; Feliu, J. M.; Herrero, E. Oxidation Mechanism of Formic Acid on the Bismuth Adatom-Modified Pt(111) Surface. *J. Am. Chem. Soc.* **2014**, *136* (38), 13110–13113.
- (31) Zhou, P.; Lv, X.; Tao, S.; Wu, J.; Wang, H.; Wei, X.; Wang, T.; Zhou, B.; Lu, Y.; Frauenheim, T.; Fu, X.; Wang, S.; Zou, Y. Heterogeneous-Interface-Enhanced Adsorption of Organic and Hydroxyl for Biomass Electrooxidation. *Adv. Mater.* **2022**, *34* (42), No. 2204089.
- (32) Verma, A. M.; Laverdure, L.; Melander, M. M.; Honkala, K. Mechanistic Origins of the PH Dependency in Au-Catalyzed Glycerol Electro-Oxidation: Insight from First-Principles Calculations. *ACS Catal.* **2022**, *12* (1), 662–675.
- (33) Mekazni, D. S.; Arán-Ais, R. M.; Ferre-Vilaplana, A.; Herrero, E. Why Methanol Electro-Oxidation on Platinum in Water Takes Place Only in the Presence of Adsorbed OH. *ACS Catal.* **2022**, *12* (3), 1965–1970.
- (34) Santiago, P. V. B.; Raju, S. P.; Akkiraju, K.; Vicente, R. A.; da Silva, M. A.; Yuan, S.; Zanchet, D.; Shao-Horn, Y.; Fernández, P. S. Perovskite Oxides as an Opportunity to Systematically Study the Electrooxidation of Alcohols and Polyols on Materials Based on Abundant Elements: Learning from the Experience Using Pure Metals and Metallic Oxides in Electrocatalysis. *ACS Appl. Energy Mater.* **2023**, *6* (13), 7025–7051.