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Water adsorption on bimetallic PtRu/Pt(111) surface alloys

Julia M. Fischer, David Mahlberg, Tanglaw Roman and Axel Groß

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Review timeline

Original submission:	4 August 2016
Revised submission:	15 September 2016
Final acceptance:	22 September 2016

Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History

RSPA-2016-0618.R0 (Original submission)

Review form: Referee 1 (Dominique Costa)

Is the manuscript an original and important contribution to its field?
Yes

Is the paper of sufficient general interest?
Yes

Is the overall quality of the paper suitable?
Yes

Quality of the paper
An excellent paper making an important contribution to the field: should be published.

Can the paper be shortened without overall detriment to the main message?
No

Do you think some of the material would be more appropriate as an electronic appendix?
No

For papers with colour figures – is colour essential?
Yes

If there is supplementary material, is this adequate and clear?
Not applicable

Are there details of how to obtain materials and data, including any restrictions that may apply?
Yes

Do you have any ethical concerns with this paper?
No

Recommendation?
Accept as is

Comments to the Author(s)
This paper presents a theoretical study of water layers adsorption on PtRu surface alloys of different compositions on Pt(111). Four surface Ru concentrations are studied: 0; 33%, 66% and 100%. It is shown that water has an increased affinity for Ru. Water keeps the hexagonal ice layer structure for all Ru concentrations but 100% for which the structure is pentagonal. An interesting dynamics study is also done, which shows that the ice structure is destroyed at room temperature, at the exception of the Pt1Ru2 alloy which provides a hexagonal Ru Template, that stabilizes the water molécules. The paper is very interesting, well written, convincing and can be published as it is.

Review form: Referee 2

Is the manuscript an original and important contribution to its field?
Yes

Is the paper of sufficient general interest?
Yes

Is the overall quality of the paper suitable?
Yes

Quality of the paper
A good paper worth publishing in Proceedings.

Can the paper be shortened without overall detriment to the main message?
No

Do you think some of the material would be more appropriate as an electronic appendix?
No

For papers with colour figures – is colour essential?
Yes

If there is supplementary material, is this adequate and clear?
Not applicable

Are there details of how to obtain materials and data, including any restrictions that may apply?
Yes

Do you have any ethical concerns with this paper?
No

Recommendation?
Accept with minor revision (please list in comments)

Comments to the Author(s)
Dear editor,

In general this is a useful and timely study, which is written with excellent clarity. However, there are some issues with regard to the setup and presentation of the results that should be considered:

- The authors say nothing about their use of k-points for the metallic system, the choice of PAW potentials or the vacuum in the cell.
- The choice of only 2 water layers in the AIMD is a little surprising - I assume that the cell has a significant vacuum here as well, so there are two interfaces in the system: water-metal and water-vacuum. Can anything useful be said when these two interfaces are in such close proximity to each other?
- I wonder if the snapshots in Fig. 3d-f (and Fig. 5d-f) would be more useful replaced by average O positions during the run?

Decision letter (RSPA-2016-0618)

08-Sep-2016

Dear Dr Gross,

On behalf of the Editor, I am pleased to inform you that your Manuscript RSPA-2016-0618 entitled "Water adsorption on bimetallic PtRu/Pt(111) surface alloys" has been accepted for publication subject to minor revisions in Proceedings A. Please find the referees' comments below.

The reviewer(s) have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the reviewer(s)' comments and revise your manuscript. Please note that we have a strict upper limit of 28 pages for each paper. Please endeavour to incorporate any revisions while keeping the paper within journal limits. Please note that page charges are made on all papers longer than 20 pages. If you cannot pay these charges you must reduce your paper to 20 pages before submitting your revision. Your paper has been ESTIMATED to be 10 pages. We cannot proceed with typesetting your paper without your agreement to meet page charges in full should the paper exceed 20 pages when typeset. If you have any questions, please do get in touch.

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- Competing interests
- Authors' contributions
- Acknowledgements
- Funding statement
- Ethics statement

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Once again, thank you for submitting your manuscript to Proceedings A and I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Best wishes
Raminder Shergill
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Proceedings A

Reviewer(s)' Comments to Author:

Referee: 1
Comments to the Author(s)
This paper presents a theoretical study of water layers adsorption on PtRu surface alloys of different compositions on Pt(111). Four surface Ru concentrations are studied: 0; 33%, 66% and 100%. It is shown that water has an increased affinity for Ru. Water keeps the hexagonal ice layer structure for all Ru concentrations but 100% for which the structure is pentagonal. An interesting dynamics study is also done, which shows that the ice structure is destroyed at room temperature, at the exception of the Pt1Ru2 alloy which provides a hexagonal Ru Template, that stabilizes the water molécules. The paper is very interesting, well written, convincing and can be published as it is.

Referee: 2
Comments to the Author(s)
In general this is a useful and timely study, which is written with excellent clarity. However, there are some issues with regard to the setup and presentation of the results that should be considered:

- The authors say nothing about their use of k-points for the metallic system, the choice of PAW potentials or the vacuum in the cell.

- The choice of only 2 water layers in the AIMD is a little surprising - I assume that the cell has a significant vacuum here as well, so there are two interfaces in the system: water-metal and water-vacuum. Can anything useful be said when these two interfaces are in such close proximity to each other?
- I wonder if the snapshots in Fig. 3d-f (and Fig. 5d-f) would be more useful replaced by average O positions during the run? Board member pre-assessment comments (if available):

Board Member
Comments to Author(s):
(There are no comments.)

Author's Response to Decision Letter for (RSPA-2016-0618)

See Appendix A.

Appendix A

Ref. Decision on RSPA-2016-0618 - Proceedings A
Title: Water adsorption on bimetallic PtRu/Pt(111) surface alloys
Authors: J. Fischer, D. Mahlberg, T. Roman, A. Gross

Dear editors of Proceedings A,

we are very pleased that both reviewers recommend publication of our manuscript and that the paper already has been accepted by Proceedings A. Referee 2 had some very helpful comments. We have carefully considered them and changed the manuscript accordingly. All the changes are described in detail below in the Reply to Referee 2.

Best regards,
Axel Gross

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Reply to Referee 1
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> This paper presents a theoretical study of water layers adsorption on PtRu surface alloys of different compositions on Pt(111). Four surface Ru concentrations are studied: 0; 33%, 66% and 100%. It is shown that water has an increased affinity for Ru. Water keeps the hexagonal ice layer structure for all Ru concentrations but 100% for which the structure is pentagonal. An interesting dynamics study is also done, which shows that the ice structure is destroyed at room temperature, at the exception of the Pt1Ru2 alloy which provides a hexagonal Ru Template, that stabilizes the water molecules. The paper is very interesting, well written, convincing and can be published as it is.

Response: We are glad that referee 1 recommends publication of our paper as is.

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Reply to Referee 2
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> In general this is a useful and timely study, which is written with excellent clarity.

Response: We really appreciate that referee 2 states that our paper "is written with excellent clarity."

> However, there are some issues with regard to the setup and presentation of the results that should be considered:
- The authors say nothing about their use of k-points for the metallic system, the choice of PAW potentials or the vacuum in the cell.

Response: We regret that we forgot to report these important technical parameters. In the revised version, we now mention them. In fact, we already mentioned that we are using PAW potentials.

We modified the second paragraph of the section on Computational details to

"Ordered surface alloys have been considered with a Ru content of 0, 1/3, 2/3 and 1 in a $\sqrt{3}\times\sqrt{3}R30^{\circ}$ geometry using a k-point sampling of 9x9x1 to replace the integration over the first Brillouin zone. The ab initio molecular dynamics (AIMD) simulations have been performed in a $2 \sqrt{3}\times2\sqrt{3}R30^{\circ}$ surface unit cell employing 5x5x1 k-points. A vacuum region of at least 15 A was chosen, depending on the number of water layers."

> - The choice of only 2 water layers in the AIMD is a little surprising - I assume that the cell has a significant vacuum here as well, so there are two interfaces in the system: water-metal and water-vacuum. Can anything useful be said when these two interfaces are in such close proximity to each other?

Response: We admit that only two water layers corresponds to a relatively thin water film. The main reason for the small number is to reduce the still significant numerical effort associated with ab initio molecular dynamics simulations. In Ref. 42, we had shown that water layers at Pt(111) assume a bulk liquid-like structure from the third layer on. On the other hand, in Ref. 18 we had shown some time ago that two water layers are sufficient to reproduce basic properties of water films on metal electrodes. We therefore replaced the last sentence of the section on Computational Details by

"The AIMD simulations were performed with the Verlet algorithm using a time step of 1 fs within the microcanonical ensemble considering two water layers. This corresponds to a rather thin film. Recent AIMD simulations of a water film on Pt(111) have revealed that at this particular electrode the water layers assume a bulk liquid-like structure from the third layer on [42]. On the other hand, previously it was shown that two water layers at close-packed metal electrodes are sufficient to reproduce basic properties of adsorbed water layers [18]. In order to limit the still high computational cost of AIMD simulations, we have therefore chosen to take into account only two layers of water."

> - I wonder if the snapshots in Fig. 3d-f (and Fig. 5d-f) would be more useful replaced by average O positions during the run?

We thank the referee for this suggestion. However, average oxygen positions are not too instructive as their mean value is rather close to the initial position. Instead, we have now added a third row of panels to Figure 3 where we show the trajectories of the oxygen atoms along the AIMD runs illustrating their displacement due to the thermal motion. Furthermore, we have added a corresponding statement in the text on page 8. We have not extended the discussion as it already covers what is shown in the added panels.