Computational study of the adsorption of benzene and hydrogen on palladium–iridium nanoalloys

Davis, Jack B.a.; Horswell, Sarah L.; Piccolo, Laurent; Johnston, Roy L.

DOI:

[10.1016/j.jorganchem.2015.04.033](https://doi.org/10.1016/j.jorganchem.2015.04.033)

License:

Other (please specify with Rights Statement)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Davis, JBA, Horswell, SL, Piccolo, L & Johnston, RL 2015, 'Computational study of the adsorption of benzene and hydrogen on palladium–iridium nanoalloys', *Journal of Organometallic Chemistry*, vol. 792, pp. 190-3.
<https://doi.org/10.1016/j.jorganchem.2015.04.033>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

NOTICE: this is the author's version of a work that was accepted for publication in *Journal of Organometallic Chemistry*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Journal of Organometallic Chemistry*, DOI: 10.1016/j.jorganchem.2015.04.033.

Eligibility for repository checked

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Computational Study of the Adsorption of Benzene and Hydrogen on Palladium-Iridium Nanoalloys

Jack B.A. Davis, Sarah L. Horswell, Laurent Piccolo, Roy L. Johnston

PII: S0022-328X(15)00245-4

DOI: [10.1016/j.jorganchem.2015.04.033](https://doi.org/10.1016/j.jorganchem.2015.04.033)

Reference: JOM 19019

To appear in: *Journal of Organometallic Chemistry*

Received Date: 30 January 2015

Revised Date: 12 April 2015

Accepted Date: 21 April 2015

Please cite this article as: J.B.A. Davis, S.L. Horswell, L. Piccolo, R.L. Johnston, Computational Study of the Adsorption of Benzene and Hydrogen on Palladium-Iridium Nanoalloys, *Journal of Organometallic Chemistry* (2015), doi: 10.1016/j.jorganchem.2015.04.033.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Computational Study of the Adsorption of Benzene and Hydrogen on Palladium-Iridium Nanoalloys

Jack B. A. Davis^a, Sarah L. Horswell^a, Laurent Piccolo^b, Roy L. Johnston^{a,*}

^a*School of Chemistry, University of Birmingham, B15 2TT, United Kingdom*

^b*Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS & Université Lyon 1, 2 avenue Albert Einstein, F-69626 Villeurbanne Cedex, France*

Abstract

The preferred chemisorption sites on a variety of palladium-iridium nanoalloys are determined for benzene and hydrogen molecules. Available sites on the surface of the nanoalloys are explored using a random-search method, directly at the density functional level of theory. These searches successfully reveal the site preference for benzene and significant nanosize effects in the chemisorption of hydrogen. It is hoped that through the study of the chemisorption properties of Pd-Ir nanoalloys, complex catalytic processes, such as tetralin hydroconversion and the preferential oxidation of CO, can be better understood.

Keywords: DFT, Palladium, Iridium, Nanoalloy, Catalysis, Benzene, Hydrogen

1. Introduction

Nanoalloys (NAs) are a class of nanomaterials composed of two or more metallic elements. These include nanoparticles (NPs), 2D-like structures, such as nanogrids and sheets, and 1D-like structures, such as nanowires and nanotubes.[1] The combination of metals in a NP results in properties which are dependent not only on size and shape,[2] but also on the composition and chemical ordering.[3] The presence of two or more metals introduces homotops, isomers differing in only the ordering of elements.[4]

Palladium-iridium is a strongly demixing alloy system[5, 6, 7]. This is reflected in the structural characteristics of the corresponding nanoalloys.[8, 9] Pd-Ir nanoalloys have been investigated previously for application in a number of catalytic processes,[10, 11, 12, 13, 14, 15, 16] including tetralin hydroconversion through selective ring opening,[14] a process which is key to understanding how to reduce particulate emissions from diesel fuel. Here it was hoped the catalytic properties of each metal would be combined in the nanoalloy catalyst. Ir has been shown to be active in C-C bond hydrogenolysis.[17] Pd shows improved hydrogen activation and thioresistance over other noble metal catalysts. Through alloying, depending on the relative proportions of metals, increased activity and selectivity can be obtained.

Understanding the role of hydrogen in tetralin hydroconversion and other reactions, such as the preferential oxidation of CO (PROX), is vital.[15, 16] Bulk Pd is the only metal at ambient temperature and hydrogen pressure to form a hydride.[18, 19] Nanosize effects on the Pd-H system have been widely studied.[19, 20] Nanosize Pd exhibits an increased hydrogen

absorption rate and decreased adsorption capacity.[21, 22] Recently, the interaction of hydrogen with Pd, Ir and Pd-Ir was probed, with nanosized-induced hydrogen absorption being reported for Ir.[23, 16] The sorption (adsorption+absorption) capacity of Pd-Ir nanoalloys was found to be strongly reduced compared with the pure NPs.[16] Furthermore, the addition of Ir to Pd inhibits the formation of Pd hydride. This is thought to be beneficial to the activity of Pd-Ir as a catalyst since the hydride is unselective in PROX.

Theoretical studies of the interaction of molecular hydrogen with nanoalloys are limited. Pd, Pt and Pd-Pt nanoparticles (NPs) have been investigated previously using density functional theory (DFT).[24, 25] Kozlov and co-workers investigated the differences between the adsorption and absorption of hydrogen atoms on Pd and Pt NPs.[25] The work was found to be in agreement with previous studies suggesting that hydrogen dissociatively adsorbs in the subsurface of Pd.

A study of the interactions between benzene and hydrogen molecules with a range of Pd-Ir nanoalloys is presented here. The nanoalloy structures are truncated octahedra (TOs), whose chemical ordering has been predicted using the Free-Energy Concentration Expansion Method with coordination-dependent bond energy variations (FCM/CBEV).[8] The FCM/CBEV lowest energy TO homotops for Pd₄Ir₃₄, Pd₈Ir₃₀ and Pd₂₀Ir₁₈, are studied alongside monometallic Pd₃₈ and Ir₃₈. Although for 38-atoms the TO is almost certainly not the global minimum, it is representative of the TO structures seen for larger Pd-Ir particles.[14]

2. Methodology

2.1. DFT

Gamma-point, spin-polarised DFT calculations were performed using VASP.[26, 27, 28, 29, 30] Projected-augmented

*r.l.johnston@bham.ac.uk

wave pseudopotentials were used with the PBEsol exchange correlation functional.[31, 32] A plane-wave basis set with a cut-off of 400 eV was used. Methfessel-Paxton smearing, with a sigma value of 0.01 eV, was used to improve metallic convergence.[33]

2.2. Search Method

To determine the site preferences for both benzene and hydrogen, a DFT-based random search method was utilised, analogous to the *ab initio* random search (AIRS) approach of Pickard et al.[34] To begin a search an initial configuration of the ligand-cluster system was generated by placing a single ligand molecule tangential to a locally minimised cluster. The random search then consisted of a fixed numbers of steps. A step in the search combined a random rotation move with a local minimisation at the DFT level.

The random rotation was performed on the cluster whilst keeping the position of the ligand molecule fixed. After each selective rotation a local minimisation was performed using VASP. These calculations were performed at 0 K and, therefore, no atom diffusion occurred. This methodology was able to sample comprehensively the available adsorption sites on the surface of the cluster.

2.3. Energetics

The adsorption energy, E_{ads} for each cluster was defined as the difference between the energy of the cluster with adsorbate, $E_{\text{cluster+ligand}}$, and the sum of the energies of the bare cluster, E_{cluster} and gas-phase ligand, E_{ligand} , as shown in equation 1.

$$E_{\text{ads}} = E_{\text{cluster+ligand}} - (E_{\text{cluster}} + E_{\text{ligand}}) \quad (1)$$

3. Results

3.1. Benzene

The Pd-Ir FCEM/CBEV TO homotop structures used in the searches are shown in Figure 1. Each clearly shows Pd segregating to the surface of the cluster, giving a variety of mono- and bimetallic adsorption sites. The segregation of Pd is favoured by the lower surface energy of Pd compared to Ir.

For each composition, local minimisations were carried out on 50 random chemisorption sites. The adsorption energies of the most favourable sites are given in Table 1. The lowest energy structures are given in Figure 2. Benzene was found to chemisorb most favourably to Ir and Ir-rich clusters, with E_{ads} of around -4.5 eV. This interaction diminishes as the proportion of Pd is increased.

The graph in Figure 3 shows the ordered chemisorption energies from each random search. The plot gives an indication as to how many inequivalent sites have been explored for each composition. Several steps taken for Pd₄Ir₃₄ and Pd₈Ir₃₀ produce non-interacting structures, shown by E_{ads} values around 0 eV. In some cases energetically equivalent minima are sampled multiple times producing steps on the plots. This is shown by the Ir₃₈ plot, which exhibits eight clearly inequivalent steps. Many of the smaller differences seen for the other compositions

Figure 1: Top views of the FCEM/CBEV lowest energy homotop structures for Pd₄Ir₃₄, Pd₈Ir₃₀ and Pd₂₀Ir₁₈ shown from left to right. Ir and Pd are shown in gold and silver, respectively.

Figure 2: Lowest energy benzene chemisorption site for each composition. Pd, Ir, C and H are shown in silver, gold, black and pink, respectively.

Figure 3: Adsorption energies for the 50 random steps taken for each nanoalloy composition in the presence of benzenes. Energies are ordered from lowest to highest.

may arise from the greater orientational flexibility of the benzene molecule.

The lowest energy site found for Pd₃₈ and Ir₃₈ was the (100) face of the TO. For Pd₄Ir₃₄ and Pd₂₀Ir₁₈ the lowest energy site was the Ir (100) face of the cluster. The lowest energy site found on Pd₈Ir₃₀ was a bimetallic (100) face but on closer inspection, the monometallic Ir (100) face had not been explored by the random search. A local minimisation was carried out with ben-

zene placed at the (100) site. This was found to be the new lowest energy site.

These results compare favourably with those from previous studies of benzene adsorption on bulk metal surfaces. The adsorption energies reported for the Ir(100) and Pd(100) surfaces are -2.88 eV and -2.03 eV, respectively.[35, 36] These are considerably larger (in absolute values) than the corresponding (111) values and explain the preference for the (100) site on the TO.[37] The E_{ads} reported for the NA clusters are considerably larger than those values reported for the bulk metal surfaces. This suggests a significant nanosize effect, especially in case of the pure Ir and Ir-rich clusters.

After adsorption, significant strain can be seen in the benzene molecule. Figure 4 shows benzene chemisorbed onto $\text{Pd}_{20}\text{Ir}_{18}$. The benzene structure is distorted with C-H bonds clearly bent away from the cluster. The amount of strain a NA can introduce into a benzene molecule could be related to its catalytic activity in the ring opening of cyclic hydrocarbons.

Table 1: The average C-C bond lengths, $R_{\text{C-C}}$, and adsorption energies, E_{ads} for benzene on the Pd, Ir and Pd-Ir clusters.

Composition	$R_{\text{C-C}} / \text{\AA}$	$E_{\text{ads}} / \text{eV}$
Ir_{38}	1.46	-4.44
$\text{Pd}_4\text{Ir}_{34}$	1.46	-4.50
$\text{Pd}_8\text{Ir}_{30}$	1.46	-4.44
$\text{Pd}_{20}\text{Ir}_{18}$	1.46	-3.87
Pd_{38}	1.41	-2.66

Figure 4: Top and side views of the lowest energy chemisorption site for benzene on $\text{Pd}_{20}\text{Ir}_{18}$.

3.2. Hydrogen

For each composition, local minimisations were carried out on 50 random chemisorption sites. The chemisorption energies and structures of the most favourable sites are given in Table 2 and figure 5.

For Pd_{38} molecular hydrogen is found to chemisorb non-dissociatively at a large number of sites on the cluster. This differs from Ir_{38} where for each site explored hydrogen is found to dissociate upon chemisorption. On the mixed clusters, the number of dissociated hydrogen molecules was found to increase as the Ir content of the cluster increased (Table 2).

The lowest energy site for each composition is found to be one in which the hydrogen molecule has dissociated. For the

Table 2: The total number of dissociated hydrogen molecules, N_{diss} , and lowest adsorption energy, E_{ads} , from 50 random search steps for hydrogen on the Pd, Ir and Pd-Ir clusters.

Composition	N_{diss}	$E_{\text{ads}} / \text{eV}$
Ir_{38}	50	-1.98
$\text{Pd}_4\text{Ir}_{34}$	50	-1.94
$\text{Pd}_8\text{Ir}_{30}$	44	-1.95
$\text{Pd}_{20}\text{Ir}_{18}$	42	-1.64
Pd_{38}	28	-1.46

Ir and Pd-Ir clusters each hydrogen atom is chemisorbed to an edge site of a (100) face. For Pd_{38} each hydrogen is found to chemisorb to a *fcc* site on a (111) face. These results correlate well with those from a previous DFT study of the bulk metal surfaces.[38] Hydrogen was found to favour the bridge sites on the Ir(100) surface, equivalent to the edge sites on the cluster. On Pd the *fcc* sites on the (111) surface were preferred, equivalent to *fcc* sites on the (111) face of the TO.

The difference in E_{ads} for a hydrogen atom on the Ir(100) bridge and Ir(111) *fcc* sites was reported as 0.3 eV. This correlates with the preference for hydrogen to chemisorb to the (100) edge sites of the Ir and Ir-rich clusters. Pd shows the opposite order with a difference in E_{ads} for the Pd(100) four-fold and Pd(111) *fcc* sites of -0.7 eV. This again correlates with the hydrogen's preference for the (111) *fcc* sites on the Pd TO.

Figure 5: Lowest energy hydrogen chemisorption site for all compositions, each with dissociated hydrogen shown in pink.

4. Conclusions

In real world catalytic processes Pd-Ir NAs are exposed to multiple reactants. Understanding the chemisorption properties of Pd, Ir and Pd-Ir clusters can aid in the full description of their catalytic properties in these complex environments. It is thought that the combination of Pd and Ir promotes PROX catalytic performance by preventing poisoning through hydrogen sorption.

In this study, significant nanosize effects are seen in the adsorption of hydrogen. Hydrogen is found to dissociate and chemisorb most strongly on pure Ir and Ir-rich clusters. On Pd and Pd-rich clusters hydrogen is often found to chemisorb associatively. The effect of composition on chemisorption is more pronounced for hydrogen than for benzene, with a greater variety of energies and differing site preferences for pure hydrogen adsorption on Pd and Ir.

The strongly segregating Pd-Ir clusters display a wide variety of sites on their surfaces. In tetralin hydroconversion in the presence of H₂S, it could be the case that iridium provides the strongest chemisorption sites for the aromatic ring, whilst the presence of Pd helps to prevent the poisoning of the catalyst because of its weaker interaction with sulphur.[39]

Future studies will include the development of automatic search techniques for the global optimisation of NAs in the presence of ligands. Theoretical work could be extended to the benzene+hydrogen reaction. It is hoped that this and future work can be used to aid in the explanation of experimental work on the Pd-Ir system.

The nanosize effects seen in Pd and Ir clusters will be further investigated. Studies will include calculating the energy barriers to hydrogen dissociation and investigating the adsorption properties of the bulk materials and clusters of a greater variety of size, shape and composition.

5. Acknowledgements

R.L.J. dedicates this paper to Mike Mingos on the occasion of his 70th birthday, with gratitude for his inspiration, encouragement and support over the past 30 years.

J.B.A.D. and R.L.J. acknowledge the Engineering and Physical Sciences Research Council, U.K. (EPSRC) for funding under Critical Mass Grant EP/J010804/1 TOUCAN: Towards an Understanding of Catalysis on Nanoalloys.

6. References

- [1] R. L. Johnston, *Atomic and Molecular Clusters*, Taylor and Francis, London, 2002.
- [2] Y. Li, G. A. Somorjai, *Nanoscale advances in catalysis and energy applications*, *Nano Letters* 10 (7) (2010) 2289–95. doi:10.1021/nl101807g. URL <http://www.ncbi.nlm.nih.gov/pubmed/20524636>
- [3] R. Ferrando, J. Jellinek, R. L. Johnston, *Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles*, *Chemical Reviews* 108 (3) (2008) 845–910. doi:10.1021/cr040090g. URL <http://www.ncbi.nlm.nih.gov/pubmed/18335972>
- [4] J. Jellinek, E. B. Krissinel, *NinAlm Alloy Clusters : Analysis of Structural Forms and Their Energy Ordering*, *Chemical Physics Letters* 258 (1996) 283–292.
- [5] P. E. A. Turchi, V. Drchal, J. Kudrnovský, *Stability and ordering properties of fcc alloys based on Rh, Ir, Pd, and Pt*, *Physical Review B* 74 (6) (2006) 064202. doi:10.1103/PhysRevB.74.064202. URL <http://link.aps.org/doi/10.1103/PhysRevB.74.064202>
- [6] B. Kolb, S. Müller, D. B. Bots, G. L. W. Hart, *Ordering tendencies in the binary alloys of Rh, Pd, Ir, and Pt: Density functional calculations*, *Physical Review B* 74 (14) (2006) 144206. doi:10.1103/PhysRevB.74.144206. URL <http://link.aps.org/doi/10.1103/PhysRevB.74.144206>
- [7] S. N. Tripathi, S. R. Bharadwaj, M. S. Chandrasekharaiah, *The Ir-Pd (Iridium-Palladium) System*, *Journal of Phase Equilibria* 12 (5) (1991) 603–605.
- [8] J. B. A. Davis, R. L. Johnston, L. Rubinovich, M. Polak, *Comparative modelling of chemical ordering in palladium-iridium nanoalloys*, *Journal of Chemical Physics*.
- [9] J. B. A. Davis, S. L. Horswell, R. L. Johnston, *Global Optimization of 8-10 Atom Palladium-Iridium Nanoalloys at the DFT Level*, *Journal of Physical Chemistry A* 118 (2014) 208–214. doi:10.1021/jp408519z. URL <http://www.ncbi.nlm.nih.gov/pubmed/24328270>
- [10] K. Persson, a. Ersson, K. Jansson, N. Iverlund, S. Jaras, *Influence of co-metals on bimetallic palladium catalysts for methane combustion*, *Journal of Catalysis* 231 (1) (2005) 139–150. doi:10.1016/j.jcat.2005.01.001. URL <http://linkinghub.elsevier.com/retrieve/pii/S002195170500014>
- [11] A. Rocha, E. Moreno, G. da Silva, J. Zotin, A. Faro, *Tetralin Hydrogenation on Dealuminated Y Zeolite-Supported Bimetallic Pd-Ir Catalysts*, *Catalysis Today* 133-135 (2008) 394–399. doi:10.1016/j.cattod.2007.12.099. URL <http://linkinghub.elsevier.com/retrieve/pii/S092058610700950>
- [12] S. Shen, T. Zhao, J. Xu, *Carbon-supported bimetallic PdIr catalysts for ethanol oxidation in alkaline media*, *Electrochimica Acta* 55 (28) (2010) 9179–9184. doi:10.1016/j.electacta.2010.09.018. URL <http://linkinghub.elsevier.com/retrieve/pii/S001346861001177>
- [13] Y. M. López-De Jesús, C. E. Johnson, J. R. Monnier, C. T. Williams, *Selective Hydrogenation of Benzonitrile by Alumina-Supported Ir-Pd Catalysts*, *Topics in Catalysis* 53 (15-18) (2010) 1132–1137. doi:10.1007/s11244-010-9546-0. URL <http://www.springerlink.com/index/10.1007/s11244-010-9546-0>
- [14] L. Piccolo, S. Nassreddine, M. Aouine, C. Ulhaq, C. Geantet, *Supported Ir-Pd Nanoalloys: Size-Composition Correlation and Consequences on Tetralin Hydroconversion Properties*, *Journal of Catalysis* 292 (2012) 173–180. doi:10.1016/j.jcat.2012.05.010. URL <http://linkinghub.elsevier.com/retrieve/pii/S002195171200150>
- [15] F. Morfin, S. Nassreddine, J. L. Rousset, L. Piccolo, *Nanoalloying Effect in the Preferential Oxidation of CO over Ir-Pd Catalysts*, *ACS Catalysis* 2 (10) (2012) 2161–2168. doi:10.1021/cs3003325. URL <http://pubs.acs.org/doi/abs/10.1021/cs3003325>
- [16] C. Zlotea, F. Morfin, T. S. Nguyen, N. T. Nguyen, J. Nelayah, C. Ricolleau, M. Lacroche, L. Piccolo, *Nanoalloying bulk-immiscible iridium and palladium inhibits hydride formation and promotes catalytic performances*, *Nanoscale* 6 (2014) 9955–9959. doi:10.1039/C4NR02836H. URL <http://pubs.rsc.org/en/content/articlepdf/2014/nr/c4nr02836h>
<http://pubs.rsc.org/en/content/articlehtml/2014/nr/c4nr02836h>
- [17] L. Piccolo, S. Nassreddine, G. Toussaint, C. Geantet, *Mechanism of Tetralin Ring Opening and Contraction over Bifunctional Ir/SiO₂-Al₂O₃ Catalysts*, *ChemSusChem* 5 (9) (2012) 1717–1723.
- [18] D. N. Jewett, A. C. Makrides, *Diffusion of hydrogen through palladium and palladium-silver alloys (1965)*. doi:10.1039/tf9656100932. URL <http://xlink.rsc.org/?DOI=tf9656100932>
- [19] T. B. Flanagan, W. A. Oates, *The Palladium-Hydrogen System*, *Annual Review of Materials Research* 21 (1991) 269–304.
- [20] A. Pundt, R. Kirchheim, *HYDROGEN IN METALS: Microstructural Aspects*, *Annual Review of Materials Research* 36 (1) (2006) 555–608. doi:10.1146/annurev.matsci.36.090804.094451. URL <http://www.annualreviews.org/doi/abs/10.1146/annurev.matsci.36.090804.094451>
- [21] C. Langhammer, V. P. Zhdanov, I. Zorić, B. Kasemo, *Size-Dependent Kinetics of Hydriding and Dehydriding of Pd Nanoparticles*, *Physical Review Letters* 104 (13) (2010) 135502. doi:10.1103/PhysRevLett.104.135502. URL <http://link.aps.org/doi/10.1103/PhysRevLett.104.135502>
- [22] P. Dibandjo, C. Zlotea, R. Gadiou, C. Matei Ghimbeu, F. Cuevas, M. Lacroche, E. Leroy, C. Vix-Guterl, *Hydrogen storage in hybrid nanostructured carbon/palladium materials: Influence of particle size and surface chemistry*, *International Journal of Hydrogen Energy* 38 (2) (2013) 952–965. doi:10.1016/j.ijhydene.2012.10.050. URL <http://linkinghub.elsevier.com/retrieve/pii/S036031991202338>
- [23] H. Kobayashi, M. Yamauchi, H. Kitagawa, *Finding hydrogen-storage capability in iridium induced by the nanosize effect*, *Journal of the American Chemical Society* 134 (2012) 6893–6895. doi:10.1021/ja302021d.
- [24] A. Lebon, A. Garcia-Fuente, A. Vega, F. Aguilera-Granja, *Hydrogen Interaction in PdPt Alloy Nanoparticles*, *The Journal of Physical Chemistry C* 116 (2011) 126–133. URL <http://pubs.acs.org/doi/pdf/10.1021/jp207329q>
<http://pubs.acs.org/doi/abs/10.1021/jp207329q>

- [25] S. M. Kozlov, H. A. Aleksandrov, K. M. Neyman, Adsorbed and Sub-surface Adsorbed Hydrogen Atoms on Bare and MgO(100) -Supported Pd and Pt Nanoparticles, *Journal of Physical Chemistry C* 118 (2014) 15242–15250.
- [26] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Physical Review B* 47 (1) (1993) 558–561.
URL http://prb.aps.org/abstract/PRB/v47/i1/p558_1
- [27] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metalamorphous-semiconductor transition in germanium, *Physical Review B* 49 (20) (1994) 14251–14269.
URL http://prb.aps.org/abstract/PRB/v49/i20/p14251_1
- [28] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science* 6 (1) (1996) 15–50.
URL <http://www.sciencedirect.com/science/article/pii/0927025696000080>
- [29] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical Review. B* 54 (16) (1996) 11169–11186.
URL <http://www.ncbi.nlm.nih.gov/pubmed/9984901>
- [30] H. J. Monkhorst, J. D. Pack, Special points for Brillouin-zone integrations, *Physical Review B* 13 (12) (1976) 5188–5192.
URL <http://www-dft.ts.infn.it/resta/tcse/old/monkhorstpack.pdf>
- [31] J. Perdew, A. Ruzsinszky, G. Csonka, O. Vydrov, G. Scuseria, L. Constantin, X. Zhou, K. Burke, Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces, *Physical Review Letters* 100 (13) (2008) 136406. doi:10.1103/PhysRevLett.100.136406.
URL <http://link.aps.org/doi/10.1103/PhysRevLett.100.136406>
- [32] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Physical Review B* 59 (3) (1999) 1758 – 1775.
URL http://prb.aps.org/abstract/PRB/v59/i3/p1758_1
- [33] M. Methfessel, A. T. Paxton, High-precision sampling for Brillouin-zone integration in metals, *Physical Review B* 40 (6) (1989) 3616–3621.
URL http://prb.aps.org/abstract/PRB/v40/i6/p3616_1
- [34] C. J. Pickard, R. J. Needs, Ab initio random structure searching., *Journal of physics. Condensed matter : an Institute of Physics journal* 23 (2011) 053201. arXiv:1101.3987, doi:10.1088/0953-8984/23/5/053201.
- [35] H. Orita, N. Itoh, Simulation of phenol formation from benzene with a Pd membrane reactor: Ab initio periodic density functional study, *Applied Catalysis A: General* 258 (2004) 17–23. doi:10.1016/j.apcata.2003.08.001.
- [36] S. Yamagishi, S. J. Jenkins, D. a. King, Benzene and its dissociation products on Ir{100}, *Journal of Physical Chemistry C* 112 (2008) 14417–14427. doi:10.1021/jp804041j.
- [37] S. J. Jenkins, Aromatic adsorption on metals via first-principles density functional theory, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 465 (June) (2009) 2949–2976. doi:10.1098/rspa.2009.0119.
- [38] P. Ferrin, S. Kandoi, A. U. Nilekar, M. Mavrikakis, Hydrogen adsorption, absorption and diffusion on and in transition metal surfaces: A DFT study, *Surface Science* 606 (7-8) (2012) 679–689. doi:10.1016/j.susc.2011.12.017.
URL <http://dx.doi.org/10.1016/j.susc.2011.12.017>
- [39] D. R. Alfonso, First-principles studies of H₂S adsorption and dissociation on metal surfaces, *Surface Science* 602 (2008) 2758–2768. doi:10.1016/j.susc.2008.07.001.

-
- A random search at the density functional level of theory is used to determine the site preference for the adsorption of benzene and hydrogen on a variety of Pd-Ir nanoalloys.
- Significant nanosize effects are seen in the chemisorption of hydrogen.
- The site preferences for both benzene and hydrogen are found to correlate with their preference on the analogous bulk surfaces.