Structure dependence of Pt surface activated ammonia oxidation

Citation for published version (APA):
Santen, van, R. A., Offermans, W. K., Ricart, J. M., Novell-Leruth, G., & Perez-Ramirez, J. (2008). Structure dependence of Pt surface activated ammonia oxidation. *Journal of Physics: Conference Series*, *117*, 012028-1/7. https://doi.org/10.1088/1742-6596/117/1/012028

DOI:
10.1088/1742-6596/117/1/012028

Document status and date:
Published: 01/01/2008

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 16. Nov. 2023

Ab initio Simulation of Crystalline Solids: History and Prospects IOP Publishing
Journal of Physics: Conference Series **117** (2008) 012028 doi:10.1088/1742-6596/117/1/012028

Structure dependence of Pt surface activated ammonia oxidation

R A[1] van Santen, W K Offermans[1], J M Ricart[2], G Novell-Leruth[2] and J Pérez-Ramírez[3]

[1] Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[2] Department of Chemical Physics and Inorganic Chemistry, University Rovira i Virgili, C/ Marcel.lí Domingo s/n, 43007 Tarragona, Spain
[3] Institute of Chemical Research of Catalonia (ICIQ) and Catalan, Institution for Research and Advanced Studies (ICREA), Avinguda Països Catalans 16, 43007, Tarragona, Spain

E-mail: r.a.v.santen@tue.nl

Abstract. Computational advances that enable the prediction of the structures and the energies of surface reaction intermediates are providing essential information to the formulation of theories of surface chemical reactivity. In this contribution this is illustrated for the activation of ammonia by coadsorbed oxygen and hydroxyl on the Pt(111), Pt(100), and Pt(211) surfaces.

1. Introduction

Computational study of ammonia activation on different surfaces of Pt has elucidated important general aspects of transition states of reactions on transition metal surfaces [1, 2, 3].

An interesting feature is the insensitivity of NH_3 and NH_2 activation to the surface structure [4]. This has been found to be related to the nature of the corresponding transition states. Whereas NH_2, the product of NH_3 dehydrogenation, preferentially adsorbs in twofold or higher coordination to the metal surface, in the transition state the nitrogen atom has not yet displaced itself from its initial atop configuration. A similar feature holds for NH formation from NH_2. In the transition state with the NH bond in NH_2 essentially broken, the nitrogen atom has not yet displaced from its original twofold coordination site, whereas NH preferentially adsorbs in a higher coordination site. Only when NH dissociates substantial differences in the activation energies are found. The lower barrier for dissociation on the (111) surface compared to that on the (100) surface is due to the difference in the repulsive interaction between the dissociating fragments. Again in the transition state the NH bond can be considered to be essentially completely broken, but in the transition state the adsorbed N atom and H atom experience a very different repulsive interaction. Whereas on the (111) surface the N-atom and H-atom, each located in different triangular surface metal atom sites, bind to the same metal atoms and therefore experience a significant repulsive interaction, the different topology of the (100) surface generates a transition state with N and H both twofold coordinated to surface metal atoms but at opposite sites of the square arrangements of the surface atoms of the (100) surface.

Here we compare the activation of ammonia by coadsorbed O or OH. It appears that on different surfaces differences in activation barrier again correlate strongly to the above mentioned feature that when the surface structure changes in the transition state, repulsive interactions tend to become very different. We will compare results of studies already partially published elsewhere [1, 2, 4]. The surfaces to be compared are the Pt(111), (100), and (211) surfaces respectively.

2. Method

Electronic structure calculations within the framework of DFT have been performed using the VASP code [5, 6, 7]. The functional from the Generalized Gradient Approximation of Perdew and Wang is used [8]. The Pt surfaces are formed by a periodical expansion, which consist of several layers of Pt atoms separated by a vacuum layer. The nudged elastic band method (NEB) with improved tangent estimate has been used to determine the minimum energy path of the surface reactions [9, 10, 11]. For details of the calculations we refer to references [1, 2].

3. Discussion

We will initiate our analysis with a comparison of the activation of adsorbed NH_x species by O and OH on the Pt(111) and Pt(100) surfaces. Figure 1 shows a comparison of the reaction energies in the absence and presence of coadsorbed reactant on the Pt(111) surface. The corresponding surface intermediates for reaction with O and OH are shown in figure 3. Figure 2 shows a comparison of reaction with co-reactants O and OH on the Pt(100) surface. The corresponding surface intermediates are shown in figure 4.

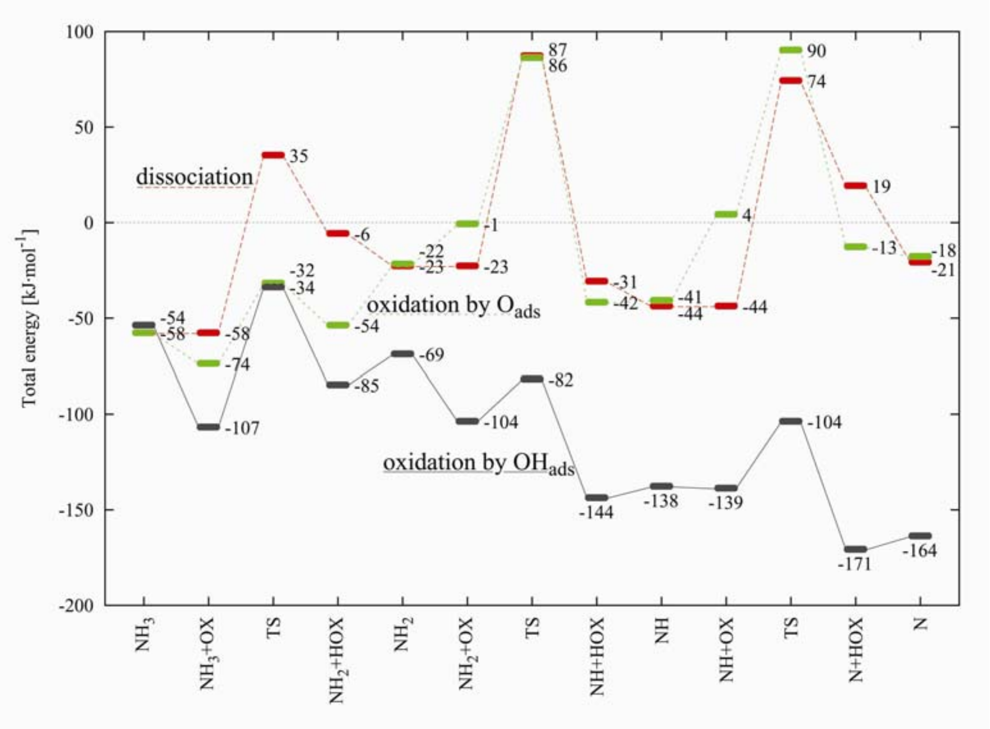

Figure 1. Reaction energy diagram of the dehydrogenation reactions of ammonia on Pt(111). All total energies are with respect to $NH_{3,gas}$, $Pt(111)_s$, 3 O_{ads} and 3 H_{ads} and are zero point energy corrected. OX or HOX on the abscissa mean oxidator or hydrogenated oxidator and can be OH, O or an empty site or their hydrogenated forms. All NH_x+(H)OX states are co-adsorbate states with lateral interactions. In all other adsorbate states, we assume no lateral interactions.

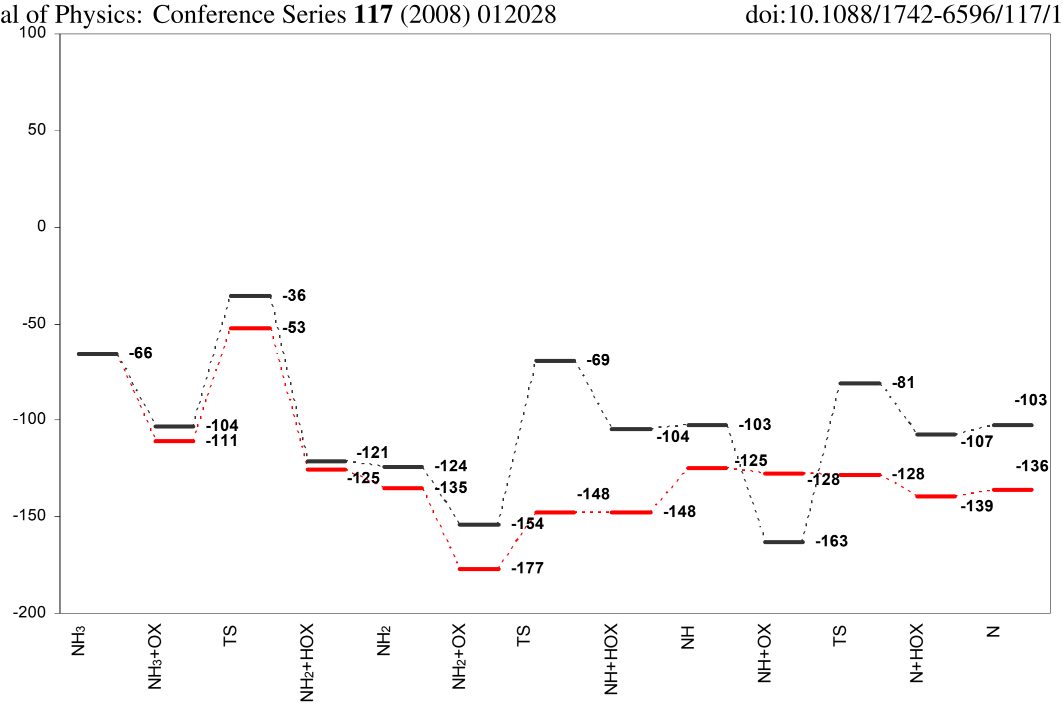

Figure 2. Reaction energy diagram for O-assisted (red) and OH-assisted (black) ammonia dehydrogenation on Pt(100). Details as in figure 1.

A remarkable observation is the opposite trend in reactivity for reaction with adsorbed O as well as OH. Whereas on the Pt(111) surface only for ammonia the reaction barrier is lowered from 93 kJ mol^{-1} to 42 kJ mol^{-1} by reaction with coadsorbed O to give NH_2 and hydroxyl, on the Pt(100) surface also reaction with coadsorbed O gives a lower barrier for adsorbed NH_2 or NH . The barriers of NH_3 dissociation with and without coadsorbed atomic oxygen are 113 kJ mol^{-1} and 58 kJ mol^{-1} respectively. On the 100 surface the barriers for NH_2 activation are 110 kJ mol^{-1} and 29 kJ mol^{-1} respectively, whereas on the (111) surface they are the same (figure 1).

This difference in reactivity is related to the difference in topology of these surfaces. Whereas on the (111) surface for these adsorbates transition states between coadsorbed NH_x and O are only realized in which sharing of product state surface fragments and surface metal atom occurs, such sharing is not necessary for the corresponding reactions on the (100) surface. The unique square arrangement of surface atoms allows for formation of transition states with reactant fragments adsorbed at opposite sites of the square so that they do not share bonding to the same surface atom. This can be observed by comparison of the reaction intermediate structures in figures 3 and 4.

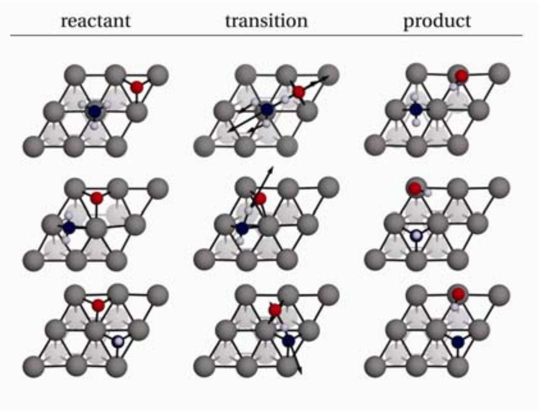

Figure 3a. Oxidation of NH_x by O_{ads} on Pt(111). The vertical projections of the unit cells show the reactant, transition and product states of the dehydrogenation reactions of $NH_{x,ads}$ by O_{ads}. The arrows in the transition states are the vertical projections of the imaginary vibration. Hence they point out the direction of the reaction path at the transition state

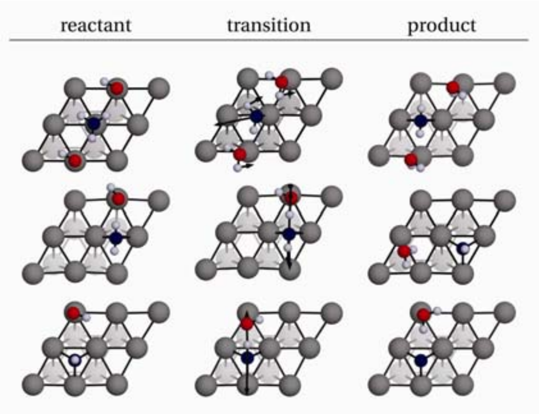

Figure 3b. Oxidation of ammonia by OH_{ads} on Pt(111). The vertical projections of the unit cells show the reactant, transition and product states of the dehydrogenation reactions of $NH_{x,ads}$ by OH_{ads}. The arrows in the transition states are the vertical projections of the direction of the reaction path at the transition state. Since we notice interactions between species of different unit cells in the NH_3+OH-reaction, we also show the mirror images of the OH_x species in this particular reaction.

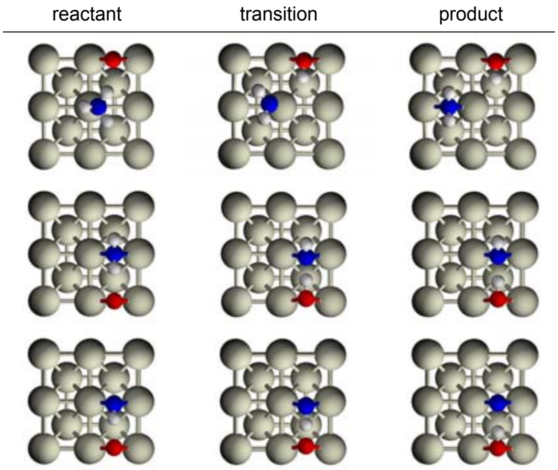

Figure 4a. Oxidation of NH_x by O_{ads} on Pt(100). The vertical projections of the unit cells show the reactant, transition and product states of the dehydrogenation reactions of $NH_{x,ads}$ by O_{ads}.

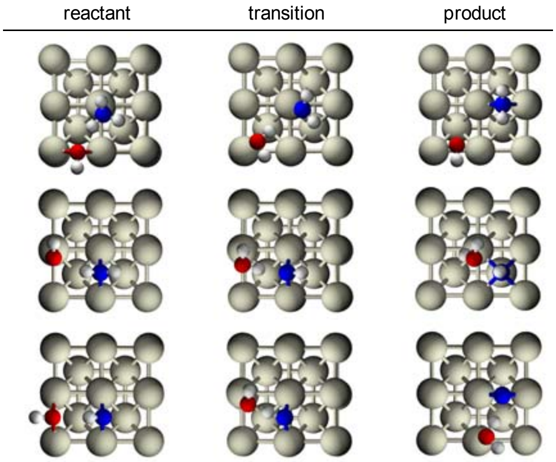

Figure 4b. Oxidation of ammonia by OH_{ads} on Pt(100). The vertical projections of the unit cells show the reactant, transition and product states of the dehydrogenation reactions of $NH_{x,ads}$ by OH_{ads}.

The increased repulsive interaction between the surface species when they bind to the same metal atom is in line with the Bond Order Conservation principle. This is a qualitative rule, used initially by Shustorovich [12], to analyze trends in surface chemical reactivity.

The weakening of the surface bonds of ad-fragments when they share bonding with the same metal atom can be intuitively understood because valence electrons of the metal atom now have to be distributed over more bonds than when no shared bonding was present. This is the reason why on the Pt(100) surface the reaction of adsorbed NH_2 and NH with adsorbed O proceeds with very low barriers, but on the (111) surface is not preferred over direct reaction with the metal surface.

Interestingly the low barriers of reaction of adsorbed NH_2 and NH with coadsorbed surface on the Pt(211) surface have the same origin. Figures 5a and 5b give the energies and surface structures of the reaction intermediates involved. One notes that all reactions in which NH_x is adsorbed at the bottom of the step and O is adsorbed at the edge of the step show very low barriers. Not only is there no sharing of metal atoms between the surface fragments in the transition state, also already before reaction adsorbed O and NH weakly interact. Therefore only a small displacement of the hydrogen atom is necessary for NH bond cleavage. In this case the presence of such agostic interaction [4] before reaction is an additional reason for the low activation barriers found. Whereas for the surface fragments NH_2 and NH the overall barrier for NH bond cleavage is lowered at the stepped surface, this is not the case for NH_3, because of its very unfavourable adsorption energy at the bottom of the step edge.

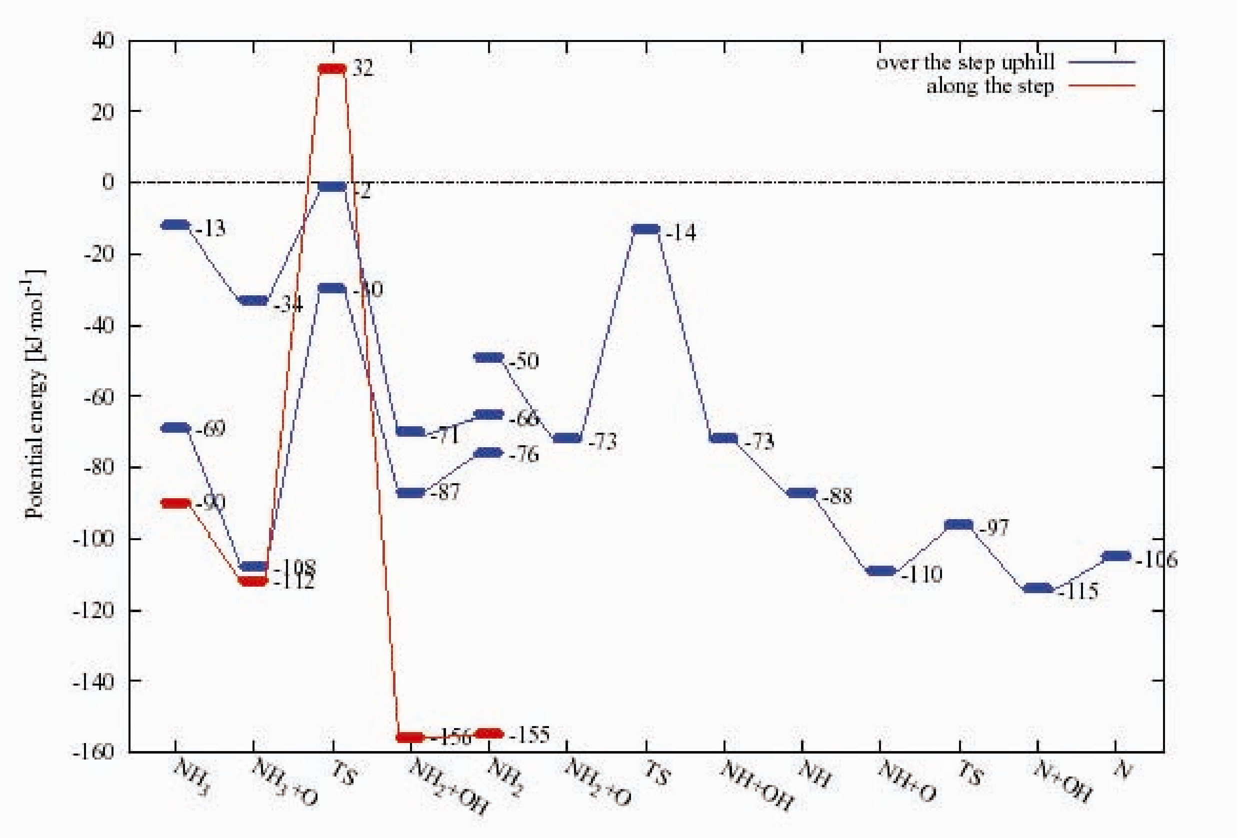

Figure 5a. Reaction energy diagram of the oxidation of NH_x by O_{ads} on Pt(211). All total energies are with respect to $NH_{3\ (g)}$, $Pt(211)_{\{s\}}$, 3 $O_{\{ads\}}$ and are not zero point energy corrected. All $NH_{\{x\}}$; (H)O co-adsorbate states are with lateral interactions. In all 'single' adsorbate states, we assume no lateral interactions.

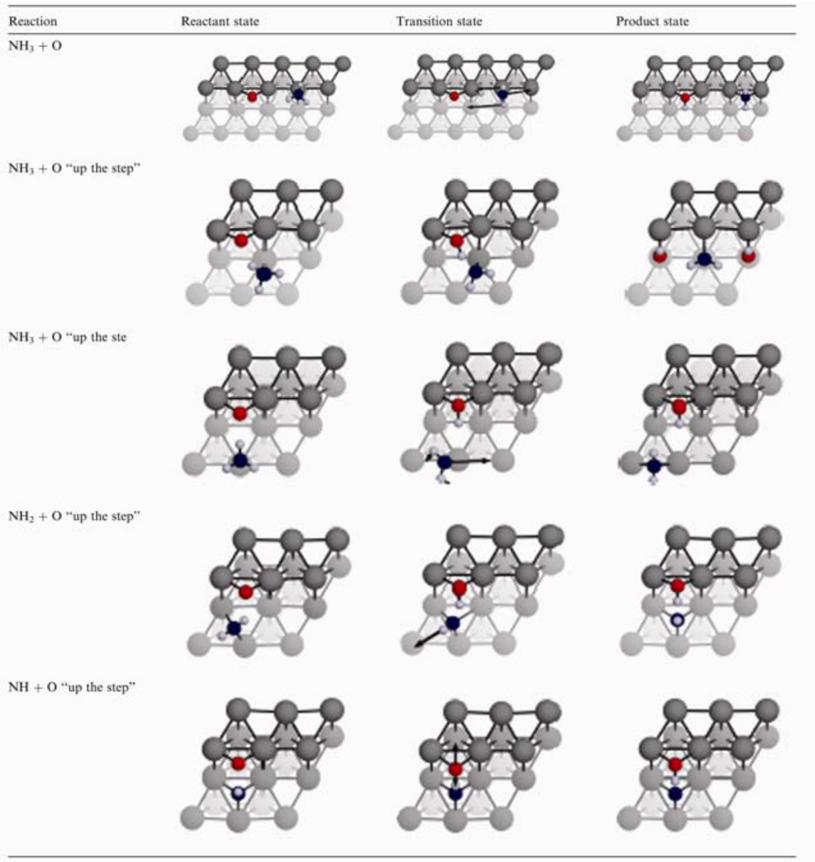

Figure 5b. Oxidation of NH_x by O_{ads} on Pt(211). The corresponding energy differences can be found in Figure 5a.

The two concepts of Bond Order Conservation and agostic interaction are also very useful to understand the remarkable difference in reactivity of the adsorbed NH_x fragments with coadsorbed hydroxyl. The key reason for the very different reactivity pattern on the (111) surface (figure 1) compared to that with coadsorbed O is low coordination of the OH reaction with the metal surface. Its preferred adsorption site is atop of the Pt surface atom. Because of this coordination mode there is no need to share chemical bonds with the same surface atom when reaction occurs with coadsorbed NH_x. Also the NH bond has to stretch over a relatively small distance in order for the OH bond to form.

Whereas on the (111) surface reaction with coadsorbed OH is more favorable than with coadsorbed O the reverse is true on the (100) surface. The explanation for this interesting contrasting behavior is the more favorable reactivity of adsorbed O on the (100) surface as well as the larger distance between reacting OH and NH_x coadsorbed on the (100) surface before reaction compared to the analogous case on the (111) surface.

4. Conclusion

The remarkable difference in surface reactivity of NH_x on the (111), (100), and (211) surfaces of Pt can be understood by in detail analysis of the structures of the reaction intermediates in their corresponding transition states. Topological differences in the location of the surface atoms cause significant structural differences of the transition states. Two surface reactivity parameters are found to be the essential descriptors of the reactions analyzed: the presence or absence of sharing of bonds with surface metal atoms and the distance over which the NH bond has to be stretched before stabilization by product bond formation occurs.

Acknowledgments

This research was financially supported by the Deutsche Forschungsgemeinschaft (DFG) in the frame of the DFG-priority program SPP 1091, “Bridging the gap between ideal and real systems in heterogeneous catalysis”. We also thank the Spanish Ministerio de Educación y Ciencia (CTQU2005-08459-C02-02 and CTQ2006-01562/PPQ) and the Catalan Government (2005SGR-00104) for financial support. JMR is indebted Prof. Pisani for precious help and guidance at the beginning of his scientific career.

References

[1] Offermans W K, Jansen A P J and van Santen R A 2006 *Surf. Sci.* **600** 1714
Popa C, Offermans W K, van Santen R A and Jansen A P J 2006 *Phys. Rev. B* **74** 155428
Imbihl R, Scheibe A, Zeng Y F, Günther S, Kraehnert, Kondatenko V A, Baerns M, Offermans W K, Jansen A P J and van Santen R A 2007 *Phys. Chem. Chem. Phys.* **9** 3522
[2] Novell-Leruth G, Valcarcel A, Clotet A, Ricart J M and Pérez-Ramírez 2005 *J. Phys. Chem. B* **109** 18061
Novell-Leruth G, Valcarcel A, Pérez-Ramírez J and Ricart J M 2007 *J. Phys. Chem. C* **111** 860
[3] Michaelides A and Hu P 2000 *J. Am. Chem. Soc.* **122** 9866
Michaelides A, Liu Z-P, Zhang C J, Alavi A, King D and Hu P 2003 *J. Am. Chem. Soc.* **125** 3704
[4] Offermans W K, Jansen A P J, van Santen R A, Novell-Leruth G, Ricart J M and Pérez-Ramírez J 2007 *J. Phys. Chem. C* **111** 17551
[5] Kresse G and Furthmüller J, 1996 *Comp. Mater. Sci.* **6** 15
[6] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
[7] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
[8] Perdew J B 1991 *Electronic Structure of Solids* (Berlin: Akademic Verlag)
[9] Jónsson H, Mills G and Jacobsen K W 1998 *Classical and Quantum Dynamics in Condensed Phase Simulations* ed B J Berne et al. (Singapore: World Scientific) pp 385–404
[10] Henkelman G, Jóhanneson and Jónsson H 2000 *Theoretical Methods in Condensed Phase Chemistry* ed S D Schwartz (Dordrecht, The Netherlands: Kluwer Academic Publishers) pp 269–300
[11] Henkelman G and Jónsson H 2000 *J. Chem. Phys.* **113** 9978
[12] Shustorovich E 1986 *Surf. Sci. Rep.* **6** 1
Shustorovich E 1990 *Adv. Catal.* **37** 101
Shustorovich E 2007 *Russ. J. Phys. Chem. B* **1** 307