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Citation for published version (APA):

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.
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Download date: 15. Mar. 2019
Structure dependence of Pt surface activated ammonia oxidation

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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$$_\text{gas}$, Pt(111)$_\text{s}$, 3 O$_{\text{ads}}$ and 3 H$_{\text{ads}}$ 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 adsorbate states, we assume no lateral interactions.
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\(_{ads}\) 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](image-url)  
*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)$_{ads}$, 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.

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