Complementary Structure Sensitive and Insensitive Catalytic Relationships

RUTGER A. VAN SANTEN*

Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, P.O Box 513, 5600 MB Eindhoven, Eindhoven University of Technology, The Netherlands

RECEIVED ON JANUARY 24, 2008

CONSPECTUS

The burgeoning field of nanoscience has stimulated an intense interest in properties that depend on particle size. For transition metal particles, one important property that depends on size is catalytic reactivity, in which bonds are broken or formed on the surface of the particles. Decreased particle size may increase, decrease, or have no effect on the reaction rates of a given catalytic system. This Account formulates a molecular theory of the structure sensitivity of catalytic reactions based on the computed activation energies of corresponding elementary reaction steps on transition metal surfaces.

Recent progress in computational catalysis, surface science, and nanochemistry has significantly improved our theoretical understanding of particle-dependent reactivity changes in heterogeneous catalytic systems. Reactions that involve the cleavage or formation of molecular π-bonds, as in CO or N_2, must be distinguished from reactions that involve the activation of σ-bonds, such as CH bonds in methane. The activation of molecular π-bonds requires a reaction center with a unique configuration of several metal

atoms and step-edge sites, which can physically not be present on transition metal particles less than 2 nm. This is called class I surface sensitivity, and the rate of reaction will sharply decrease when particle size decreases below a critical size.

The activation of σ chemical bonds, in which the activation proceeds at a single metal atom, displays a markedly different size relationship. In this case, the dependence of reaction rate on coordinative unsaturation of reactive surface atoms is large in the forward direction of the reaction, but the activation energy of the reverse recombination reaction will not change. Dissociative adsorption with cleavage of a CH bond is strongly affected by the presence of surface atoms at the particle edges. This is class II surface sensitivity, and the rate will increase with decreasing particle size. Reverse reactions such as hydrogenation typically show particle-size-independent behavior. The rate-limiting step for these class III reactions is the recombination of an adsorbed hydrogen atom with the surface alkyl intermediate and the formation of a σ-type bond.

Herein is our molecular theory explaining the three classes of structure sensitivity. We describe how reactions with rates that are independent of particle size and reactions with a positive correlation between size and rate are in fact complementary phenomena. The elucidation of a complete theory explaining the size dependence of transition metal catalysts will assist in the rational design of new catalytic systems and accelerate the evolution of the field of nanotechnology.
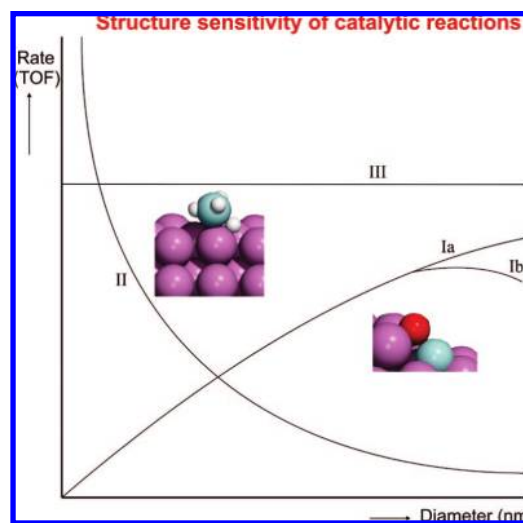
Introduction

Advances in nanomaterials research are bringing a new perspective to several fields of technology.[1] This is especially the case for heterogeneous catalysis that uses high surface area materials often activated by small transition metal particles. Most important is the possibility to study catalytic performance on well defined particles in the nanosize range as has been demonstrated by Somorjai[2] and Bezemer et al.[3]
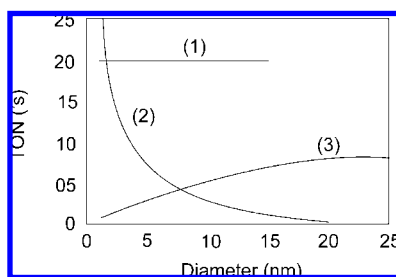
FIGURE 1. The three different kinds of structure sensitivity–particle size relationship plotted as turnover number for selected reactions versus particle size: (1) benzene hydrogenation on Pt/SiO$_2$; (2) ethane hydrogenolysis on Pt/SiO$_2$, (3) CO hydrogenation on Ru/Al$_2$O$_3$[8] (adapted from Che and Bennett, Figure 7).[7]

Progress in computational catalysis[4,5,6b] has generated a detailed picture of reaction paths for surface chemical reactions. This can be used to study in detail their dependence on structural changes when particle size varies.

In the particle size regime between 2 and 20 nm, three types of reactivity change can be distinguished.[7,8] This is illustrated in Figure 1. The rate of some reactions, normalized per exposed metal surface atom, decreases sharply when particle size decreases below a critical value. Other reactions are independent of particle size; their rate uniformly increases with decreasing particle size or may even show a maximum. This remarkable dependence of catalytic rate on dispersion of catalytically active particles has been known for nearly half a century. Boudart[9] coined the term structure sensitive and insensitive reactions.

The nature of the chemical substrate bond that is activated determines which surface atom rearrangement provides the lowest activation energy. This novel insight provides the basis for a classification of structure sensitive and insensitive reactions. Surprisingly, for some reactions different structural dependence appears to be complementary, depending on whether a bond is broken or formed.

In the next section, a short discussion of the different reactivity-length scale regimes of transition metal particles is given to justify the use of surface science data to predict reactivity of transition metal nanoparticles. Then in the following sections, we will review some key observations relevant to the molecular theory of surface structure sensitivity.

Particle Size Length Scale Regimes

There are different length scale regimes for transition metal particles in relation to their chemical reactivity (Figure 2). In transition metal particles with a size less than 1 nm, one cannot distinguish interior from exterior surface atoms. Such clusters often reconstruct when in contact with adsorbing molecules and atoms. They react typically as a molecule. Their
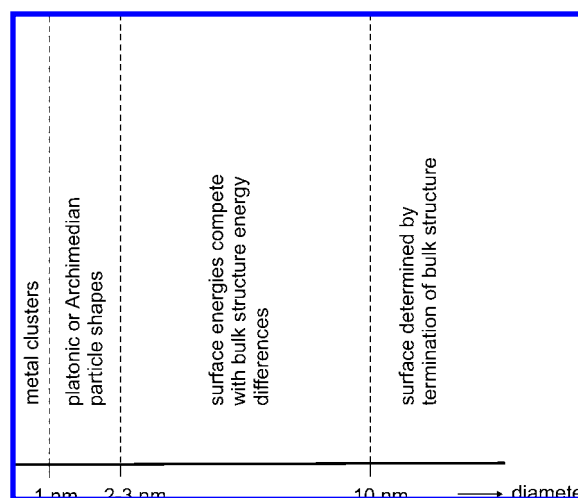

FIGURE 2. Structure–stability regimes of transition metal particles (schematic).
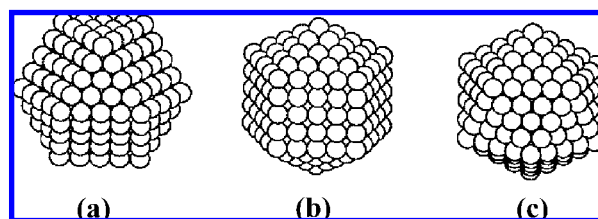

FIGURE 3. (a) Archimedian cuboctahedron, (b) Archimedian decahedron, and (c) Platonic icosahedron.

reactivity can be directly related to their orbital structure, which varies strongly with number of atoms.[10] The energy difference $\delta\varepsilon$ of the molecular orbitals varies approximately as

$$\delta\varepsilon \approx \frac{E_F}{N} \tag{1}$$

E_F is the Fermi level (i.e., highest occupied molecular orbital energy), and N is the number of atomic orbitals that participate in forming the chemical bond. For clusters of alkali metal atoms, the quantum size effect $\delta\varepsilon$ becomes on the order of kT for particles on the order of 100 atoms, which is about 1.5 nm.[11] For clusters dominated with d-type atomic orbitals, this occurs already for smaller clusters. Such small metal clusters can be distributed on a microporous support and can be shown to be highly reactive.[12]

Between 1 and 3 nm, the number of surface atoms increases over the number of interior atoms. The shape of the clusters is often that of the ideal Platonian structure, composed of similar regular polyhedra, or Archimedian bodies, built from different but regular polyhedra (Figure 3). At the upper boundary of this particle size regime, the number of surface atoms becomes less than the number of bulk atoms.

The particle size variations of relevance to the structure sensitivity of heterogeneous catalytic reactions are typically in
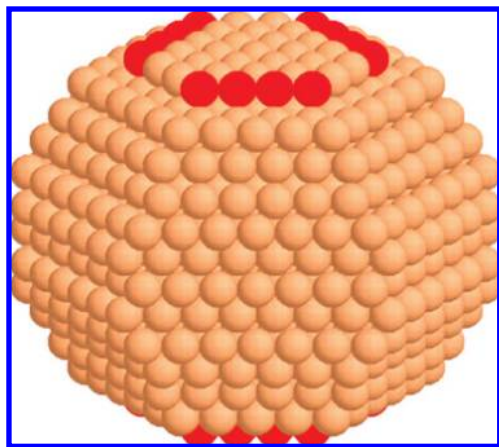
FIGURE 4. A typical calculated Ru particle with an average diameter of 2.9 nm. Atoms that belong to active B5 sites are shown in red.[16] From Honkala, K. et al. *Science* **2005**, *307* (5709), 555 (ref 16). Reprinted with permission from AAAS.

the size domain of 2−20 nm. On the surfaces of such particles apart from terrace, corner, and edge sites, also step sites can form (Figure 4). Also in the size regime 3−10 nm, the interior atoms in the bulk may not yet have a structure similar to the corresponding most stable bulk structure.[13a] An example is the structure of small Co particles that have the fcc structure instead of the more stable low-temperature hcp structure.[13b] The relative stability of different surface geometries then competes with the energy differences of different bulk structures.

At least for particles with a significant d-valence electron density at the Fermi level, the chemical reactivity of the surface of nanometer-sized particles can be considered similar to that of a surface site of the same structure at an extended surface. The strong electronic interactions with the adsorbate wash out the finer details of the surface local density of state distributions.[14,6] Therefore insights into reactivity−site dependencies obtained from surface science studies can be used to explain particle size dependent effects in heterogeneous catalysis.

Chemical Reactivity as a Function of Particle Size

A seminal early contribution was made by van Hardeveld and van Monfoort,[15] who noted unique step-edge type sites (B5 sites, Figure 4)[16] on particles with the shape of incomplete octahedra. For a crystal of octahedral shape, they identified a critical size of around 2 nm. Smaller particles cannot accommodate the B5 sites. They proposed that B5 sites are necessary for N_2 activation. Many years later, surface science studies by Zambelli et al.[17] and computational studies by the group

of Nørskov[18] confirmed the uniqueness of such sites for the dissociation of NO and N_2 at the surface step edges of Ru(0001).

More recently computational and experimental studies by Honkala et al.[16] explained the maximum in the rate of ammonia synthesis catalyzed by dispersed Ru particles as due to the requirement for the B5 sites proposed by van Hardeveld and van Montfoort. This work followed earlier surface science studies by Spencer et al.[19] who demonstrated for the same reaction the need for unique C7 sites present on the Fe(111) surface. Such sites have a very similar structure to the B5 site. Interestingly Topsoe et al.[20] had earlier demonstrated that the activity of ammonia synthesis catalysts correlated with the area of the Fe(111) surface.

We will discuss below that, as first noted by Hammer and Nørskov,[4] such step-edge structure dependence of dissociative adsorption is quite general for the cleavage of the π bonds of diatomic molecules as CO, N_2, O_2, or NO.

Computational evidence for activation of CO at B5 sites is provided by the low value of the activation energy of 65 kJ/mol for CO dissociation found on the corrugated $(11\bar{2}1)$[21] surface of Ru compared with 210 kJ/mol at the Ru(0001) terrace[22a] and similar results on Co surfaces.[23]

Hydrogenolysis reactions of alkanes with cleavage of σ C−C bonds are prototype reactions that increase in rate with decreasing particle size.[9,24] Tai et al.[25] report increased reactivity of 3 nm size Pd particles compared with surface terrace atoms. Catalytic reactions that involve CH bond activation of methane on group VIII metals also show increases in normalized conversion rate with decreasing particle size.[26]

The dramatic effect of different degrees of coordinative unsaturation of catalyst surface atoms on hydrocarbon conversion reactions has also been demonstrated by Somorjai.[27] Surfaces with a high fraction of kink sites showed for isobutane the highest selectivity to hydrogenolysis versus isomerization to n-butane. The latter is the preferred reaction for less reactive terraces with atoms of lower coordination. On such surfaces, the rate of CH bond activation is decreased and hence C−C bonds remain less accessible for bond cleavage. Calculations by Watwe et al.[28] illustrate the large decrease in activation barrier of the σ type C−C bond cleavage reaction from ∼173 kJ/mol on the (111) terrace of Pt to 102 kJ/mol along the (100) edge of the stepped Pt(211) surface. In the case of C−C bond cleavage, the activation energy at the edge atoms is decreased for the forward as well as backward reaction, because of the stabilized preactivation states by agostic interactions. An additional elegant example of such a barrier

decrease for the forward as well as backward reaction is the $CH_{3,ads}$ to $CH_{2,ads}$ conversion of methane fragments shown on Ru.[22b]

Especially studies of alloys of a group VIII metal and catalytically inert metals such as group IB or other metals indicated for hydrogenolysis the need for large surface ensembles.[29] Also an early single crystal study on Pt(111) covered with Bi by Campbell et al.[30] indicated a large ensemble requirement for dehydrogenation of cyclic hydrocarbons.

Ensemble effect theory is challenged by the recent awareness of the importance of the reactive edge atoms for such reactions. For instance a very elegant experiment by Bengaard et al.[31] demonstrated the importance of edge atoms at steps of a Ni(111) surface; addition of a small amount of Au poisoned the edge sites for methane activation.

Transition State Analysis

The three classes of surface sensitivity shown in Figure 1 relate to the different types of chemical bonds activated in a particular reaction. The two types of bonds that we have to distinguish are π bonds, as in diatomic molecules as CO or N_2, or σ bonds such as the CH bond in a hydrocarbon, NH bond in ammonia, or OH bond of water. Analysis of activation energy−reaction free energy relationships as a function of reaction site topology show revealing differences in behavior for the two different types of chemical bonds.[32] In the case that a linear relationship is found, such correlations are called Brønsted−Evans−Polanyi (BEP) relations:[4,6b,33]

$$\delta E_{act} = \alpha \delta E_{react} \quad (0 < \alpha < 1) \qquad (2)$$

In the BEP relation, δE_{act} is the change in the activation energy and δE_{react} the change in reaction energy of an elementary reaction step.

It appears that for π bond activation, only a linear BEP relation is found as long as activation is compared on surfaces of different metals of the same topology. For example, linear relationships are found when activation of N_2 on the {111} surfaces of the group VIII metals is compared or N_2 activation at a similar step site (Figure 5).[34a]

Similar BEP plots have been produced for CO and NO by the group of Hafner[35] and the group of Liu and Hu.[34b,c] The value of the BEP parameter α for the forward dissociation reaction is usually ∼0.9, implying a near complete cleavage of the molecular bond in the transition state. Note that the backward recombination reaction now is rather insensitive with respect to change of metal. This is due to microscopic reversibility:

$$E_{react} = E_{act}(forward) - E_{act}(backward) \qquad (3)$$

and hence, consequent on eq (2),

$$\delta E_{act}(backward) = -(1 - \alpha)\delta E_{react} \qquad (4)$$

For CO[23,36] and also for NO[18b,37,38] (representing molecules with a π bond), it is found that the activation energies for the forward dissociation reaction as well as the backward recombination reaction both decrease when reaction at different sites is compared. A BEP type relation is not valid when reactions at different sites are compared. This is shown in Figure 6A,B for the dissociation of CO on a terrace and step site of Ru(0001) and for NO on a stepped and nonstepped surface of Pt(111).

As is schematically illustrated in Figure 7, this is quite different for the activation of a CH σ bond as in CH_4. Values of activation energy changes for terraces and step and kink sites is given in Table 1. For this reaction structural changes around the activating metal atom give a BEP relation between activation energy and reaction energy change.[18,22,32,37] Interestingly BEP type behavior of the CH activation of hydrocarbons on Pt(111) has already been established experimentally by Campbell et al.[30]

The reason for the different behavior of methane compared with CO is that CH activation occurs over a single metal atom (Figure 8). A change in local environment around the catalytically reactive center does not affect the transition state structure but will change the reactivity of the surface metal atom.

To illustrate the difference in the reactivity of the surface atoms, in Table 2 the activation energy for CH_4 activation is dissected into the sum of first E_{str}, the gas-phase deformation
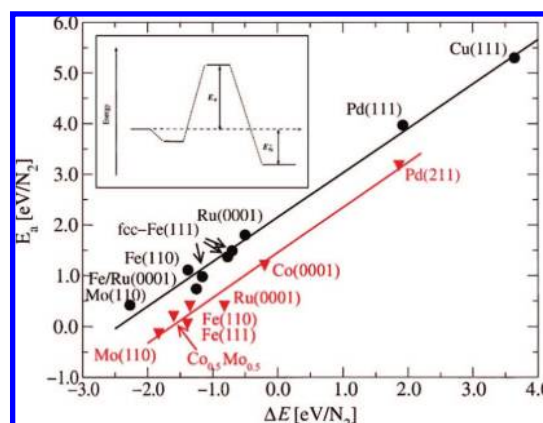

FIGURE 5. The calculated activation energies (transition state potential energies) for N_2 dissociation (E_a) on a range of metal surfaces plotted as a function of the adsorption energy for two nitrogen atoms (E_{N^*}). All energies are relative to N_2(g). Results for both close-packed surfaces (●) and more open surfaces are shown (▼). The inset shows a sketch of the energetics for the N_2 dissociation reaction.[34a] From Z.-P. Liu et al. *Appl. Catal., A.* **2001**, *114*, 8244−8247, (ref 34a). Reprinted with permission from Elsevier.
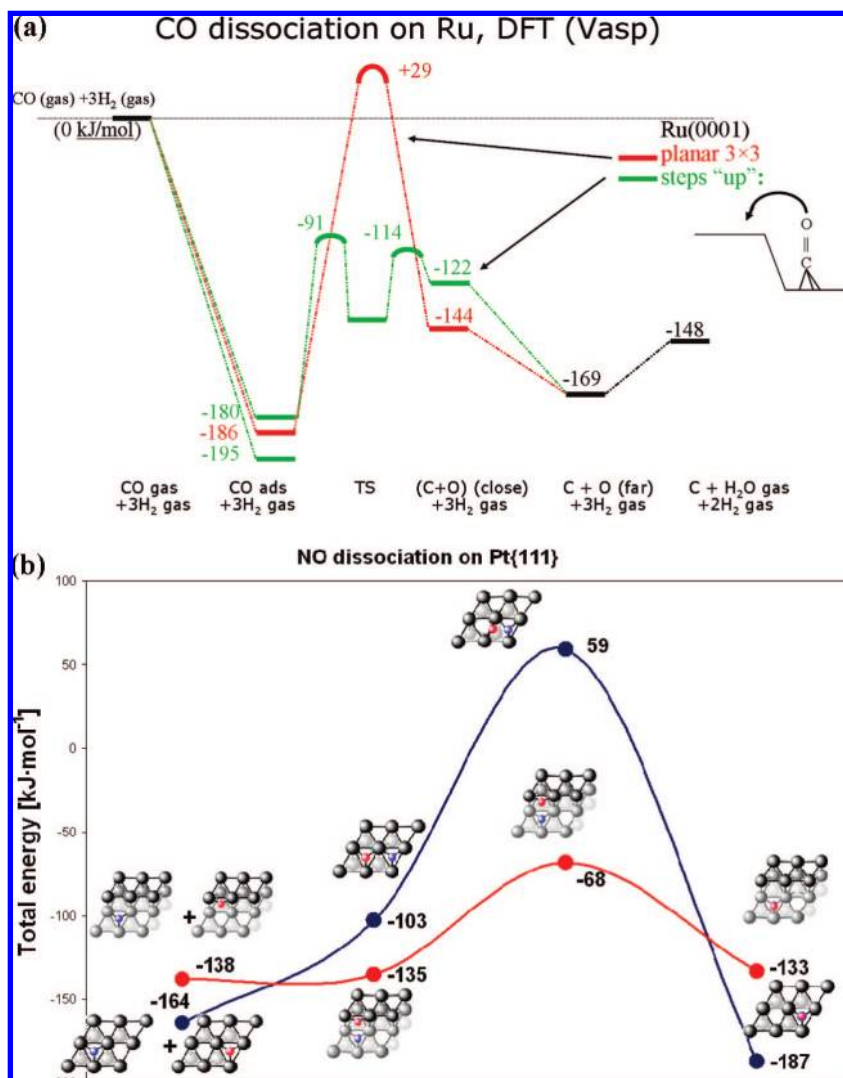
FIGURE 6. Reaction energy diagram (a) for CO activation on terrace and step of Ru(0001) surface from DFT-VASP calculations[36] and (b) for NO activation and recombination on terrace and step of Pt(111) surface from DFT-VASP calculations.[6b]
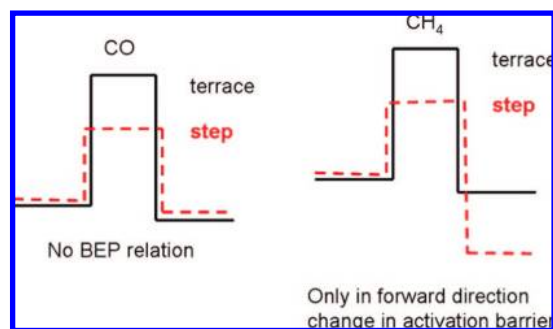

FIGURE 7. Activation energy−reaction energy relations for CO and CH$_4$ activation as a function of structure (schematic).

energy, and second ΔE_{int}, the interaction energy of a strained molecule with the surface atom. Note the similarities of E_{str} and the large differences in ΔE_{int}.[39,40]

Liu and Hu[32] were the first to make the key observation, illustrated in Figure 7, that whereas for methane the activa-

TABLE 1. Comparison of CH$_4$ Activation Energies (kJ/mol)

Ru(0001)[a]	76
Ru(1120)[b]	56
Rh(111)[c]	67
Rh step[c]	32
Rh kink[c]	20
Pd(111)[c]	66
Pd step[c]	38
Pd kink[c]	41
Pd atom[d]	5

[a] Ciobica et al.[22a] [b] Ciobica et al.[22b] [c] Liu and Hu.[32] [d] Diefenbach et al.[39]

tion energy of the forward dissociation reaction is strongly structure sensitive, the reverse reaction in which adsorbed methyl is hydrogenated then has to be only mildly structure insensitive.

Reactions also tend to have different rates when catalyzed by different surface terraces. This implies the type of structural sensitivity to which Balandin's multiplet theory refers.[41]
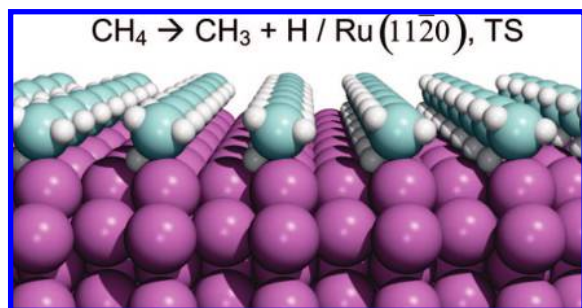
FIGURE 8. Transition state structure of CH_4 on corrugated Ru(11$\bar{2}$0) surface from VASP-DFT calculation.[22b]

TABLE 2. Methane Activation by a Metal Atom and Metal Surface

	E_{str}	E_{int}
Pd atom[a]	216	−221
Rh(111)[b]	200	−130

[a] Diefenbach et al.[39] [b] Bunnik and Kramer.[40]

In the work of Somorjai,[27] referred to earlier, several elegant examples of this behavior can be found.

A computational example is the recently discovered difference of the reactivity of ammonia activated by coadsorbed oxygen on Pt(111) and Pt(100) terraces.[42,43] Activation of ammonia by oxygen on (100) surfaces proceeds with substantially lower barriers than directly without coadsorbed oxygen (Figure 9).

The crucial difference between reactions at a (111) surface and (100) surface is that the square arrangement of the metal atoms on the (100) surface enables formation of transition states in which the fragments bind to opposite sides of the Pt multiplet square of the (100) surface (Figure 10). This reduces the repulsive interaction between reaction fragments that will occur for transition states typical of the (111) surface, that have to share a metal atom.[6,44] A similar result has been found by Ge and Neurock.[37]

Sometimes reactions at step edges have the same topological advantage as those at the (100) surface. Figure 11A,B illustrates this for activation of NH_{ads}. Whereas activation by O_{ads} on Pt(111) has a high barrier since binding to the same metal atom has to be shared in the transition state, lower barriers on (100) and (211) Pt surfaces occur because in the transition state no binding with the same surface metal atom has to be shared.[45]

Complementary Structure Sensitive Relations

We now will use the linear activation energy−reaction energy relationships discussed above to predict particle size dependence for π and σ bond activation reactions (Figure 12).
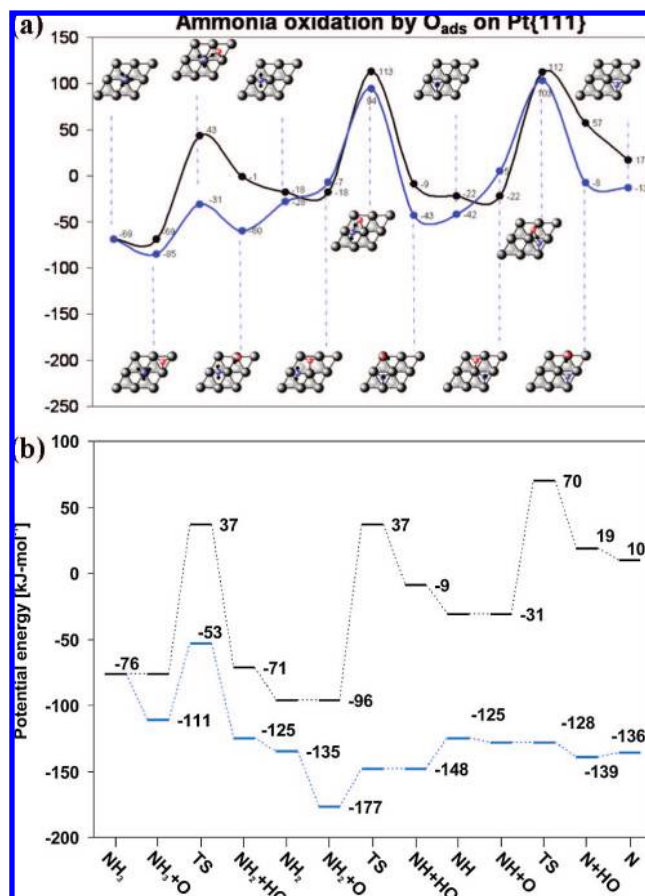

FIGURE 9. Comparison of (a) reaction energy diagrams of ammonia activation with (blue) and without (black) oxygen on Pt(111) surface. In structures nitrogen is blue and oxygen is red. (b) reaction energy diagrams of ammonia activation with (blue) and without (black) oxygen on Pt(100) surface (after Offermans et al. and van Santen et al.).[42,43]
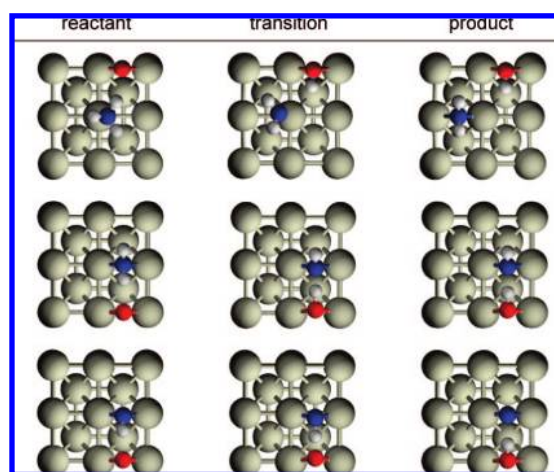

FIGURE 10. Oxidation of NH_x by O_{ads} on Pt(100). The vertical projections of the unit cells show the reactant, transition, and product states of the dehydrogenation reactions of $NH_{x,ads}$ by O_{ads}.[43]

Class I type behavior occurs for reactions in which the rate-limiting step involves the formation or dissociation of a π type
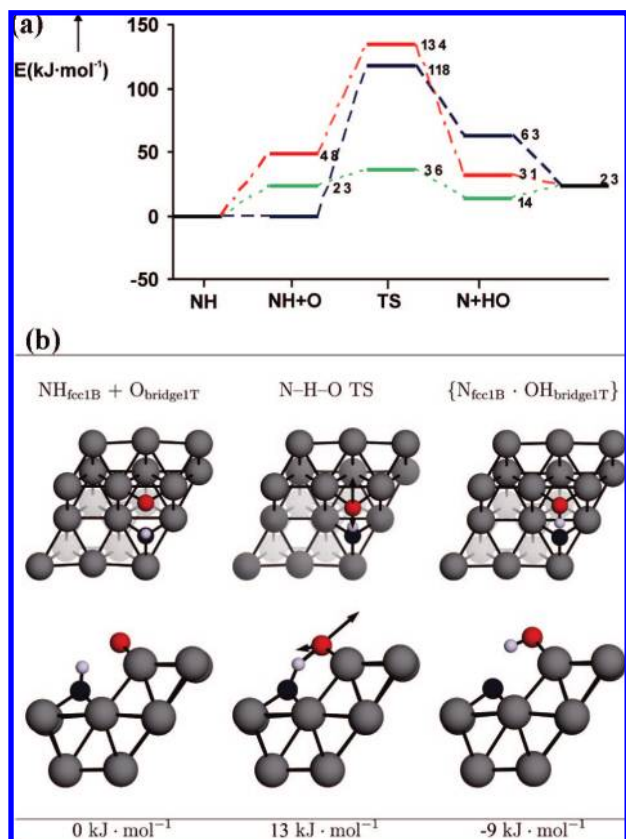
FIGURE 11. (a) Activation of NH_{ads} on Pt(111) without (blue lines) and with coadsorbed O (red lines). A comparison is made with reaction of NH_{ads} with O_{ads} on Pt(211) (green dots). (b) Structures and relative energies of NH_{ads} and O_{ads} along {211} Pt step (after Imbihl et al.).[45]
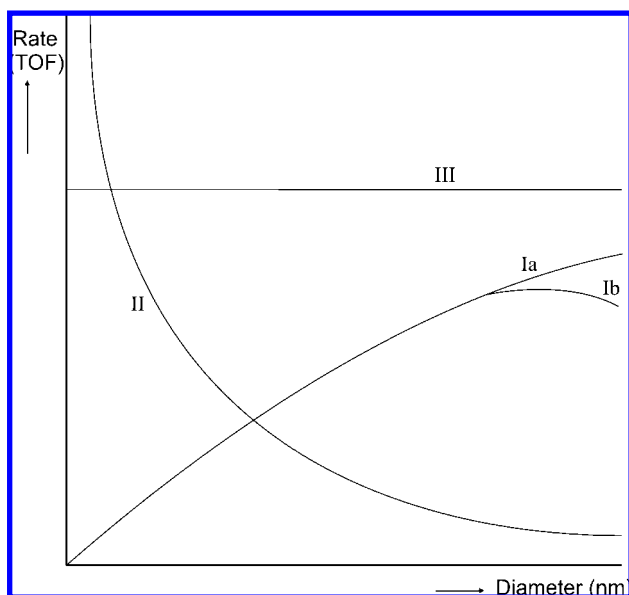

FIGURE 12. The three classes of structure sensitivity.

chemical bond. The rate may show a maximum (Ib) or may uniformly decline (Ia) as a function of decreasing particle size. The prototype reaction is dissociation of the CO or N_2 chem-

ical bond. We have discussed earlier that such π bond activation requires step-edge sites in which molecules are activated through multiple contact with several surface atoms. Such step sites are geometrically not possible below a particular particle size. The relative probability of such edge sites at the edge of a particle shows a maximum as a function of particle size.

Note that the reactivity of such a B5 site is larger near a particle edge than as part of surface terraces, because of the larger degree of coordinative unsaturation of metal atoms at the edge sites.

In agreement with this analysis, the Fischer–Tropsch reaction, which forms long chain hydrocarbons from CO, has also been found to show class I behavior.[3,46] Interestingly for Co, the conversion rate shows a sharp decline below particle sizes of 6 nm.[46] This is consistent with CO activation at double step-edges instead of single step-edge sites. Interestingly for methanation such double step-edge site activation of CO has been recently proposed.[47]

The relative number of the coordinative unsaturated edge and corner atoms will increase with decreasing particle size.

The upward shift of the average position of the d-valence electron density with coordinative unsaturation correlates with the increase in the adsorption energies of the adsorbed atoms or molecules.[4,48] This upward shift of the average d-valence electron band energy is due to increasing localization of valence electrons on the surface atom.[49,44] It explains the larger reactivity of edge and corner atoms compared with the terrace atoms. It agrees with the increased adsorption energy of CO for small Pd particles as measured by Shaikhutdinov et al.[50]

Methane activation is the prototype reaction of class II type behavior, which shows a uniform increase in reaction rate with decreasing particle size. The reverse reaction of adsorbed hydrogen recombining with adsorbed alkyl species is independent of particle size changes, and this class III type behavior is typical for transition metal catalyzed hydrocarbon hydrogenation reactions, consistent with the proposal that addition of adsorbed hydrogen to adsorbed alkyl is the rate-limiting step in olefin hydrogenation.[51]

The remarkable hypothesis that emerges from this analysis is that we now find that class II structural sensitivity and class III structural insensitivity are complementary. They are the reverse sides of the same coin. They both are typical for σ bond activation but correspond to dissociative bond cleavage and complementary associative bond formation reactions, respectively.

Ammonia activation behaves very differently from CH_4 with respect to surface structural differences. Computational studies show that activation of NH_3 and NH_2 has the same barriers on
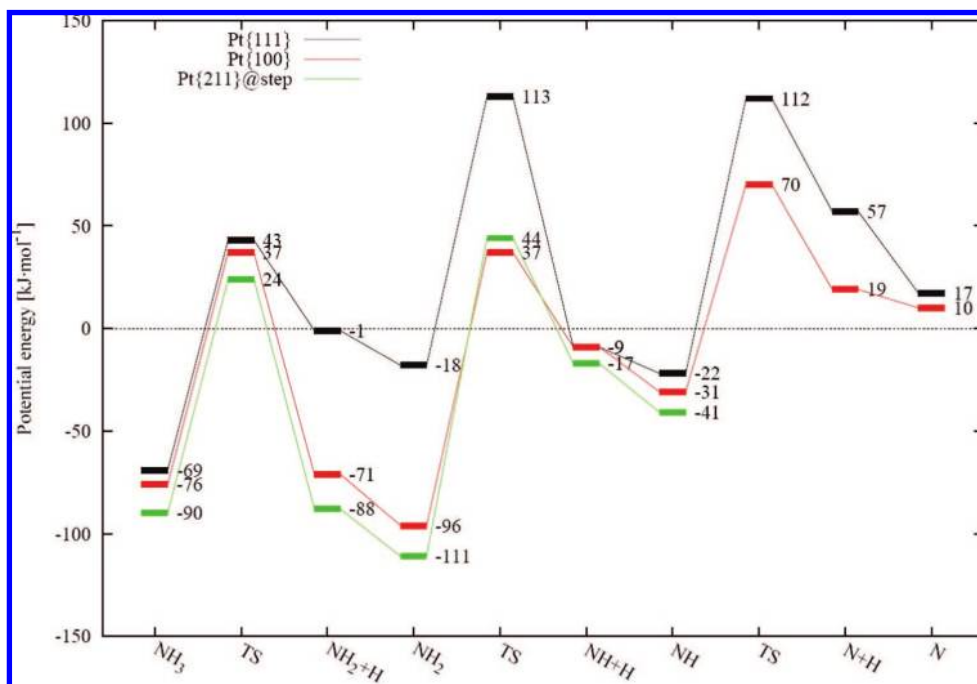
FIGURE 13. Reaction energy diagram of the NH_x ($x = 1-3$) dissociation on Pt{100} and Pt{111} and at the step of Pt{211}. Data is not zero point energy corrected.[52a]

the Pt(100) and (111) terraces. Also on surface edges the barriers do not change (Figure 13).[52a] As for methane, activation of ammonia and its fragments occurs at a single metal atom or a small surface atom ensemble. The difference in structure dependence relates to the nature of the reaction coordinate. At the transition state, the NH bond is nearly broken, but the nitrogen atom position is still close to the reactant state.

As is observed from Figure 13, the reverse reactions of NH and NH_2 hydrogenation now show large barrier differences.[52a] Again a complementary structure sensitivity–insensitivity relationship is found, but it is different from methane activation. Now hydrogenation of surface NH_x fragments is strongly structure dependent (class Ia, Figure 12).

The structure dependence of ammonia activation is dramatically different from that of methane, because of the availability of the lone-pair electrons of ammonia.[52b] The differences observed in the structure sensitivity of methane and ammonia activation are consistent with early experiments by Rostrup-Nielsen.[53]

Conclusion

On the basis of the accumulation of computed activation energies of many elementary reactions on transition metal surfaces with varying structures, it appears to be possible to formulate a molecular theory of structure sensitivity. This paper formulates such a theory. It is not only important to identify the essential structural parameters, but it is as impor-

tant to distinguish different types of activation processes. It depends on the nature of the chemical bond that is activated.

An important discovery is the complementary nature of structure sensitive and insensitive behavior of reactions in which σ bonds are activated.

For activation of π bonds, a steep decrease in the reactivity is predicted when particle sizes decrease below a particular size.

BIOGRAPHICAL INFORMATION

Rutger Anthony van Santen received his Ph.D. in theoretical chemistry in 1971, from the University of Leiden. After a post-doctoral stay at SRI, California, he joined Shell, Amsterdam, as a research chemist. In 1988, he became Professor of Catalysis at the Eindhoven University of Technology. In 1991, he became the director of The Netherlands Institute of Research in Catalysis, and in 2005, he was appointed the Royal Netherlands Academy of Science and Arts Professor. He is a member of the Royal Dutch Academy of Arts and Sciences and the American National Academy of Engineering. Professor van Santen has been active in many national and international catalysis research programs and organizations. He is the author or editor of 14 books, over 600 research papers, and 16 patents and has been awarded several national and international awards and visiting professorships. His main research interest is the molecular mechanistic understanding of catalytic reactions.

REFERENCES

1 Ozin, G. A.; Arsenault, A. C. *Nanochemistry*; Royal Society of Chemistry: Cambridge U.K., 2006.

2 Somorjai, G. A.; Tao, F.; Park, J. Y. The nanoscience revolution: Merging of colloid science, catalysis and nanoelectronics. *Top. Catal.* **2008**, *47*, 1–14.

3 Bezemer, G. L.; Bitter, J. H.; Kuipers, H. P. C. E.; Oosterbeek, H.; Hollewijn, J. E.; Xu, X.; Kapteijn, F.; van Dillen, A. J.; de Jong, K. P. Cobalt particle size effects in the Fischer−Tropsch reaction studied with carbon nanofiber supported catalysts. *J. Am. Chem. Soc.* **2006**, *128*, 3956–3964.

4 Hammer, B.; Nørskov, J. Theoretical surface science and catalysis - calculations and concepts. *Adv. Catal.* **2000**, *45*, 71–129.

5 Nillson, A.; Pettersson, L. G. M.; Nørskov, J. K. *Chemical Bonding at Surfaces and Interfaces*; Elsevier: Amsterdam, The Netherlands, 2008.

6 (a) van Santen, R. A. *Theoretical Heterogeneous Catalysis*; World Scientific: Singapore, 1991. (b) van Santen, R. A.; Neurock, M. *Molecular Heterogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 2006.

7 Che, M.; Bennett, C. O. The influence of particle size on the catalytic properties of supported metals. *Adv. Catal.* **1989**, *36*, 55–172.

8 Henry, C.; Chapon, C.; Giorgio S.; Goyhenex, C. Size effect in heterogeneous catalysis: A surface science approach. In *Chemisorption and Reactivity on Supported Clusters and Thin Films*; Lambert, R. M., Pacchioni G., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997; pp117−152.

9 Boudart, M. Catalysis by supported metals. *Adv. Catal. Relat. Subj.* **1969**, *20*, 153–166.

10 (a) *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999, Vols *1−3*. (b) *Molecular Clusters of the Main Group Elements*; Driess, M., Nöth, H., Eds.; Wiley-VCH: Weinheim, Germany, 2004.

11 (a) Knight, W. D.; Clemenger, K.; de Heer, W. A.; Saunders, W. A.; Chou, M. Y.; Cohen, M. L. Electronic shell structure and abundances of sodium clusters. *Phys. Rev. Lett.* **1984**, *52*, 2141–2143. (b) Taylor, K. J.; Pettiette-Hall, C. L.; Cheshnovsky, O.; Smalley, R. E. Ultraviolet photoelectron spectra of coinage metal clusters. *J. Chem. Phys.* **1992**, *96*, 3319–3329.

12 Argo, A. M.; Odzak, J. F.; Lai, F. S.; Gates, B. C. Observation of ligand effects during alkene hydrogenation catalyzed by supported metal clusters. *Nature* **2002**, *415*, 623–626.

13 (a) Upperbrink, J.; Wales, P. J. Structure and energetics of model metal clusters. *J. Chem. Phys.* **1992**, *96*, 8520–8534. (b) Kitakami, O.; Sato, H.; Shimada, Y.; Sato, F.; Tanaka, M. Size effect on the crystal phase of cobalt fine particles. *Phys. Rev. B* **1997**, *56*, 13849–13854.

14 (a) Koutechky, J. Contribution to the theory of the surface electronic states in the one-electron approximation. *Phys. Rev.* **1957**, *108*, 13–18. (b) Grimley, T. B. Wave mechanics of the surface bond in chemisorption. In *Advances in Catalysis*; Eley, D. D., Selwood, P. W., Weisz, P. B., Eds.; Academic Press: New York, 1960; Vol. 12, pp 1−30. (c) Newns, D. M. Self-consistent model of hydrogen chemisorption. *Phys. Rev.* **1969**, *178*, 1123–1135.

15 van Hardeveld, R.; van Montfoort, A. The influence of crystallite size on the adsorption of molecular nitrogen on nickel, palladium and platinum: An infrared and electron-microscopic study. *Surf. Sci.* **1966**, *4*, 396–430.

16 Honkala, K.; Helleman, A.; Remediakis, I. N.; Logadottir, A.; Carlsson, A.; Dahl, S.; Christensen, C. H.; Nørskov, J. K. Calculations relating the rate of ammonia synthesis to the size distribution of ruthenium catalyst nanoparticles aid in the design of this catalyst. *Science* **2005**, *307*, 555–558.

17 Zambelli, T.; Winterlin, J.; Trost, J.; Ertl, G. Identification of the "active sites" of a surface-catalyzed reaction. *Science* **1996**, *273*, 1688–1690.

18 (a) Dahl, S.; Logadottir, A.; Egeberg, R. C.; Larsen, J. H.; Chorckendorff, I.; Törnqvist, E.; Nørskov, J. K. Role of step in N₂ Activation on Ru(0001). *Phys. Rev. Lett.* **1999**, *83*, 1814–1817. (b) Hammer, B. Bond activation at monatomic steps: NO dissociation at corrugated Ru(0001). *Phys. Rev. Lett.* **1999**, *83*, 3681–3684.

19 Spencer, N. O.; Schoonmaker, R. C.; Somorjai, G. A. Iron single crystals as ammonia synthesis catalysts: Effect of surface structure on catalyst activity. *J. Catal.* **1982**, *74*, 129–135.

20 Topsoe, H. N.; Topsoe, N.; Bohlbro, H.; Dumesic, A. Supported iron catalysts: particle size dependence of catalytic and chemisorptive properties. In *Studies in Surface Science and Catalysis 7a: Proceeding of the 7th International Congress on Catalysis*; Seiyama, T., Tanabe, K., Eds.; Elsevier Pub.: Amsterdam, 1981; pp 247−265.

21 Shetty, S. G.; Jansen, A. P. J.; van Santen, R. A. CO dissociation on the Ru(112̄1) surface *J. Phys. Chem.*, published online August 19, http://dx.doi.org/10.1021/jp801754n.

22 (a) Ciobica, I. M.; Fréchard, F.; van Santen, R. A.; Kleijn, A. W.; Hafner, J. A DFT study of transition states for C-H activation on the Ru(0001) surface. *J. Phys. Chem. B* **2000**, *104*, 3364–3369. (b) Ciobica, I. M.; van Santen, R. A. A DFT study of CHₓ chemisorption and transition states for C−H activation on the Ru(112̄0) surface. *J. Phys. Chem. B* **2002**, *106*, 6200–6205.

23 Ge, Q.; Neurock, M. Adsorption and activation of CO over flat and stepped Co Surfaces: A first principles analysis. *J. Phys. Chem. B.* **2006**, *110*, 15368–15380.

24 (a) Lam, Y.; Sinfelt, J. Cyclohexane conversion on ruthenium catalysts of widely varying dispersion. *J. Catal.* **1976**, *42*, 319–322. (b) Boudart, M., Djega-Mariadassou. G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University Press: Princeton, NJ, 1984.

25 Tait, S. L.; Dohnálek, Z.; Campbell, S. L.; Kay, B. D. Methane adsorption and dissociation and oxygen adsorption and reaction with CO on Pd nanoparticles on MgO(100) and on Pd(111). *Surf. Sci.* **2005**, *591*, 90–107.

26 (a) Wei, J.; Iglesia, E. Mechanism and site requirements for activation and chemical conversion of methane on supported Pt clusters and turnover rate comparisons among noble metals. *J. Phys. Chem. B* **2004**, *108*, 4094–4103. (b) Wei, J.; Iglesia, E. Reaction pathways and site requirements for the activation and chemical conversion of methane on Ru-based catalysts. *J. Phys. Chem. B* **2004**, *108*, 7253–7262. (c) Wei, J.; Iglesia, E. Structural requirements and reaction pathways in methane activation and chemical conversion catalyzed by rhodium. *J. Catal.* **2004**, *225*, 116–127.

27 (a) Somorjai, G. A. Surface science view of catalysis: The past, present and future. In *Proceedings of the 8th International Congress on Catalysis*; Verlag Chemie: Berlin, 1984; Vol. 1 (Plenary Lectures), p 113. (b) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons, Inc.: New York, 1994.

28 Watwe, R. M.; Cortright, R. D.; Nørskov, J. K.; Dumesic, J. A. Theoretical studies of stability and reactivity of C₂ hydrocarbon species on Pt clusters. *J. Phys. Chem. B* **2000**, *104*, 2299–2310.

29 (a) Ponec, V. Selectivity in catalysis by alloys. *Catal. Rev. - Sci. Eng.* **1975**, *11* (1), 41–70. (b) Ponec, V.; Sachtler, W. M. H. Reactions of hexane isomers on nickel/copper alloys. In *Proceedings of the 5th International Congress on Catalysis*; Hightower, J. W., Ed.; North-Holland: Amsterdam, The Netherlands, 1972; Vol. 1, pp 645−657. (c) Sachtler, W. M. H.; van Santen, R. A. Surface composition and selectivity of alloy catalysts. *Adv. Catal.* **1977**, *26*, 69–119. (d) Ponec, V. Selectivity in catalysis by metals and alloys. *Progr. Surf. Membr. Sci.* **1979**, *13*, 1–85.

30 Campbell, C. T.; Campbell, J. M.; Dalton, P. J.; Henn, F. C.; Rodriguez, J. A.; Seimanides, S. G. Probing ensemble effects in surface reactions. 1. Site-size requirements for the dehydrogenation of cyclic hydrocarbons on platinum(111) revealed by bismuth site blocking. *J. Phys. Chem.* **1989**, *93*, 806–814.

31 Bengaard, H. S.; Nørskov, J. K.; Sehested, J.; Clausen, B. S.; Nielsen, L. P.; Molenbroek, A. M.; Rostrop-Nielsen, J. R. Steam reforming and graphite formation on Ni catalysts. *J. Catal.* **2002**, *209*, 365–384.

32 Liu, Z.- P.; Hu, P. General rules for predicting where a catalytic reaction should occur on metal surfaces: A density functional theory study of C−H and C−O bond breaking/making on flat, stepped, and kinked metal surfaces. *J. Am. Chem. Soc.* **2003**, *125*, 1958–1967.

33 Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*; Wiley: New York, 1996.

34 (a) Dahl, S.; Logadottir, A.; Jacobsen, C. J. H.; Nørskov, J. K. Electronic factors in catalysis: Rhe Volcano curve and the effect of promotion in catalytic ammonia synthesis. *Appl. Catal., A* **2001**, *222*, 19–29. (b) Liu, Z. - P.; Hu, P. General trends in CO dissociation on transition metal surfaces. *J. Chem. Phys.* **2001**, *114*, 8244–8247. (c) Liu, Z. - P.; Hu, P. General trends in the barriers of catalytic reactions on transition metal surfaces. *J. Chem. Phys.* **2001**, *115*, 4977–4980.

35 (a) Gajdoš, M.; Hafner, J.; Eichler, A. Ab initio density-functional study of NO adsorption on close-packed transition and noble metal surfaces: II. Dissociative adsorption. *J. Phys.: Condens. Matter* **2006**, *18*, 41–54. (b) Gajdoš, M.; Eichler, A.; Hafner, J. CO adsorption on close-packed transition and noble metal surfaces: Trends from ab initio calculations. *J. Phys.: Condens. Matter* **2004**, *16*, 1141–1164.

36 Ciobica, I. M.; van Santen, R. A. Carbon monoxide dissociation on planar and stepped Ru(0001) surfaces. *J. Phys. Chem. B* **2003**, *107*, 3808–3812.

37 Ge, Q.; Neurock, M. Structure dependence of NO adsorption and dissociation on platinum surfaces. *J. Am. Chem. Soc.* **2004**, *126*, 1551–1559.

38 (a) Loffreda, D.; Simon, D.; Sautet, P. Structure sensitivity for NO dissociation on palladium and rhodium surfaces. *J. Catal.* **2003**, *213*, 211–225. (b) Loffreda, D.; Simon, D.; Sautet, P. Molecular and dissociative chemisorption of NO on palladium and rhodium (100) and (111) surfaces: A density-functional periodic study. *J. Chem. Phys.* **1998**, *108*, 6447–6457.

39 Diefenbach, A.; de Jong, G. Th.; Bickelhaupt, F. M. Activation of H—H, C—H, C—C and C—Cl bonds by Pd and PdCl⁻. Understanding anion assistance in C—X bond activation. *J. Chem. Theory Comput.* **2005**, *1*, 286–298.

40 Bunnik, B. S.; Kramer, G. J. Energetics of methane dissociative adsorption on Rh{111} from DFT calculations. *J. Catal.* **2006**, *242*, 309–318.

41 (a) Balandin, A. A. The theory of heterogeneous catalytic reactions. The multiplet hypothesis. Model for dehydrogenation catalysis. *Z. Phys. Chem.* **1929**, *132*, 289–316. (b) Balandin, A. A. Splitting of organic compounds by catalytic hydrogenation over nickel. The role of the catalyst in heterogeneous catalysis. *Z. Phys. Chem.* **1929**, *133*, 167–194. (c) Balandin, A. A. Splitting of organic compounds by catalytic hydrogenation over nickel. The role of the catalyst in heterogeneous catalysis. *Adv. Catal.* **1969**, *19*, 1–210.

42 Offermans, W. K.; Jansen, A. P. J.; van Santen, R. A. Ammonia activation on platinum {111}: A density functional theory study. *Surf. Sci.* **2006**, *600*, 1714–1734.

43 van Santen, R. A.; Offermans, W. K.; Ricart, J. M.; Novell-Leruth, G.; Pérez-Ramírez; J. Structure dependence of Pt surface activated ammonia oxidation. *J. Phys.: Conf. Ser.* **2008**, *117*, 012028.

44 van Santen, R. A.; Neurock, M. Theory of surface chemical reactivity. *Russ. J. Phys. Chem. B* **2007**, *1*, 261–291.

45 Imbihl, R.; Scheibe, A.; Zeng, Y. F.; Günther, V. S.; Kraehnert, R.; Kondratenko, V. A.; Baerns, M.; Offermans, W. K.; Jansen, A. P. J.; van Santen, R. A. Catalytic ammonia oxidation on platinum: mechanism and catalyst restructuring at high and low pressure. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3522–3540.

46 Xiao, C.; Lai, Z.; Wang, T.; Kou, Y.; Yan, N. Aqueous-phase Fischer—Tropsch synthesis with a ruthenium nanocluster catalyst. *Angew. Chem., Int. Ed.* **2007**, *46*, 1–5.

47 Andersson, M. P.; Abild-Pedersen, F.; Remediakis, I. N.; Bligaard, T.; Jones, G.; Enbæk, J.; Lytken, O.; Horch, S.; Nielsen, J. H.; Sehested, J.; Rostrup-Nielsen, J. R.; Nørskov, J. K.; Chorkendorff, I. Structure sensitivity of the methanation reaction: H₂-induced CO dissociation on nickel surface. *J. Catal.* **2008**, *255*, 6–19.

48 Mavrikakis, M.; Hammer, B.; Nørskov, J. K. Effect of strain on the reactivity of metal surfaces. *Phys. Rev. Lett.* **1998**, *81*, 2819–2822.

49 Gross, A. Reactivity of bimetallic systems studied from first principles. *Top. Catal.* **2006**, *37*, 29–39.

50 Schaikhutdinov, S.; Heemeier, M.; Hoffmann, J.; Meusel, I.; Richter, B.; Bäumer, M.; Kuhlenbeck, H.; Libuda, J.; Freund, H.-J.; Oldman, R.; Jackson, S. D.; Konvicka, C.; Schmid, M.; Varga, P. Interaction of oxygen with palladium deposited on a thin alumina film. *Surf. Sci.* **2002**, *501*, 270–281.

51 (a) Neurock, M.; van Santen, R. A. A first principles analysis of C—H bond formation in ethylene hydrogenation. *J. Phys. Chem. B* **2000**, *104*, 1127–11145. (b) Neurock, M.; Pallasana, V.; van Santen, R. A. The importance of transient states at higher coverages in catalytic reactions. *J. Am. Chem. Soc.* **2000**, *122*, 1150–1153.

52 (a) Offermans, W. K.; Jansen, A. P. J.; van Santen, R. A.; Novell-Leruth, G.; Ricart, J. M.; Pérez-Ramírez, J. Ammonia dissociation on Pt{100}, Pt{111}, and Pt{211}: A comparative density functional theory study. *J. Phys. Chem. B* **2007**, *111*, 17551–17557. (b) Crawford, P.; Hu, P. The importance of hydrogen's potential-energy surface and the strength of the forming *R*-H bond in surface hydrogenation reactions. *J. Chem. Phys.* **2006**, *124*, 044705.

53 Rostrup-Nielsen, J. R. Activity of nickel catalysts for steam reforming of hydrocarbons. *J. Catal.* **1973**, *31*, 173–199.