Size-Dependent Oxidation Mechanism of Supported Pd Nanoparticles**

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Nanometer-sized metal particles on oxide surfaces have numerous technological applications, particularly in the field of heterogeneous catalysis.[1,2] Many catalysts applied in the chemical industry for emission control or in energy technology are based on finely dispersed noble-metal aggregates on oxides. But is the surface of these metal aggregates truly metallic under reaction conditions? This seemingly elementary question turns out to be very difficult to answer. The reason is that the influence of the reactant atmosphere on the surface structure, morphology, and composition may be rather complex. Especially in the case of oxygen-containing environments, the situation turns out to be particularly intricate. Many different oxygen species may be present even on simple single-crystal surfaces, including various types of chemisorbed oxygen (i.e. oxygen adsorbed above the first atomic layer of the metal), subsurface oxygen (i.e. oxygen incorporated into the first layers of metal atoms), thin surface oxides (i.e. very thin structures consisting of oxygen and metal-ion layers), and bulk oxides.[3–16] The puzzling role of these multiple species in reaction kinetics is a major challenge for microscopic studies in catalysis, and the related questions are currently the subject of intensive discussion (see e.g.[17–19]).

For small particles on support materials, the situation is even more complex. These particles expose multiple sites, including different facets, edges, corners, and defects; they may show modified lattice constants and electronic structures; and they may show substantial interactions with the support. All of these effects may have an influence on the thermodynamic and kinetic aspects of the formation of the different oxide species and their reactivity.

In a recent communication[20] we reported on a new oxidation and oxygen-storage mechanism for supported metal nanoparticle systems. For Pd crystallites on Fe_3O_4, initial oxidation of the metal was found to be largely dominated by the formation of a thin Pd oxide layer at the particle/support interface, which is substantially stabilized by the support. The formation and depletion of this interface oxide layer is reversible, providing the system with the ability to store and release large amounts of oxygen without major modifications of the remaining surface of the metal particle.

Here we show that this oxidation mechanism gives rise to pronounced particle-size effects: For small particles, full oxidation of the Pd particles occurs easily, but the total oxygen-storage capacity is limited by the small number of Pd atoms per unit of support surface area. For large particles, on the other hand, the Pd loading may be large, but strong kinetic hindrance inhibits Pd oxidation and, therefore, the oxygen-storage process. As a result, the supported Pd system shows a pronounced maximum of the oxygen-storage capacity at intermediate particles sizes. This size-dependent oxidation behavior and oxygen-storage functionality may be an important contribution to a microscopic-level understanding of the reaction kinetics on nanoparticle systems.

The experimental approach providing these insights is summarized in Figure 1. Briefly, we employed well-defined supported model catalysts, which were characterized in detail at the atomic level using surface-science techniques.[21–25] As a first step, particle size, morphology, and structure of these model surfaces were studied by scanning tunneling microscopy (STM). Subsequently, their reaction kinetics were probed quantitatively in a fully remote-controlled multimolecular beam (MB) experiment.[26–29] With this combination of STM and MB techniques we could obtain detailed information on the reaction kinetics as a function of the particle size and structure.

In the work presented here, we focused on Pd nanoparticles prepared in situ under ultrahigh-vacuum (UHV) conditions on an ordered Fe_3O_4 film.[30] Structure and adsorption properties of the support[30,31] and the Pd particles[20,32,33] were investigated previously. Size and density of the Pd particles can be varied within a wide range by choosing the appropriate preparation conditions. In this study, we varied the particle size between approximately 2 nm and 100 nm (corresponding to aggregates containing approximately 10^2 to 10^8 Pd atoms per particle) by changing the Pd loading (amount of Pd metal deposited per unit of support surface area). STM images of some representative samples are shown in Figure 2. Apart from the variations in particle size, it can be seen that in general the particles display a well-defined crystalline morphology. They grow in (111) orientation on the support and are terminated mainly by (111) facets as well as by a minor fraction (around 20%) of (100) side facets. Typically, the aspect ratio (height/diameter) is about 1:4 (for more details on the growth and particle morphology see Ref. [33]). The systems investigated were stabilized by thermal annealing followed by oxidation and reduction cycles prior to the experiments (see the Supporting Information). This procedure provided to a perfectly stable surface under the conditions of all kinetic experiments presented below.

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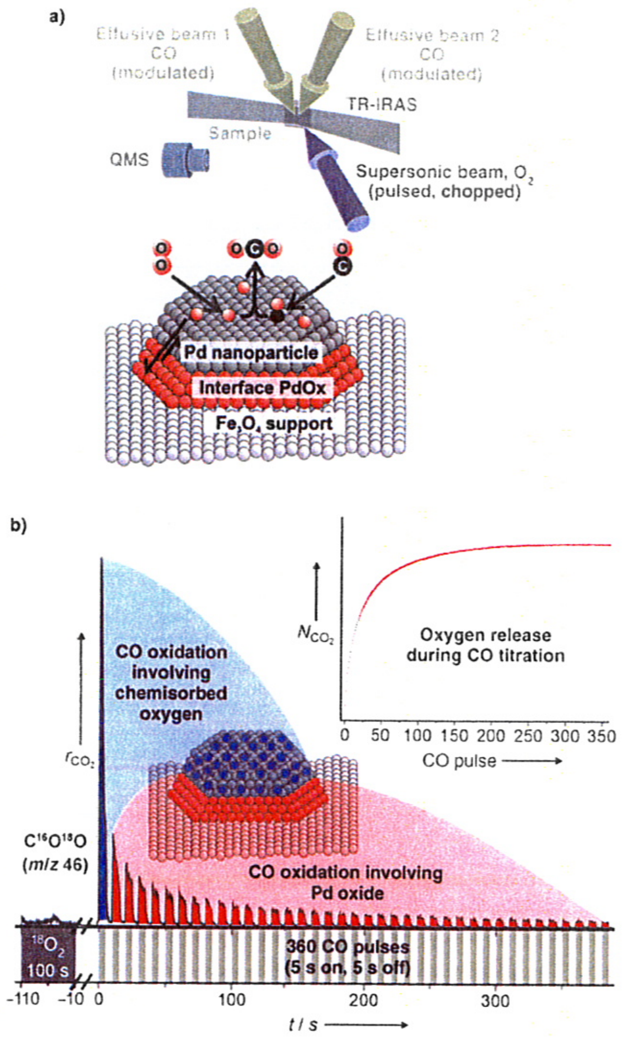

Figure 1. a) Schematic representation of the molecular beam experiment and the model catalyst surface used in this study; b) pulsed CO titration experiment on 7-nm Pd particles on Fe_3O_4 at 500 K. First, the sample was exposed to an oxygen pulse (100 s, ≈130 L). After a short delay time (10 s), 360 CO pulses (5 s on-time (≈3 L), 5 s off-time) were applied to withdraw the oxygen stored in the model catalyst in the form of CO_2. The CO_2 formation rate (r_{CO_2}) was recorded in the gas phase and integrated over the pulses (N_{CO_2}: integral CO_2 yield, inset) to determine the oxygen-storage capacity.

To probe the total oxygen-storage capacity of the Pd particles (oxygen chemisorption on metallic Pd and Pd oxide formation), a remote-controlled MB titration experiment was performed using modulated O_2 and CO beams (see Figure 1). Initially, the model surface was exposed to a pulse of oxygen. After a short delay time, the surface oxygen was titrated by pulses of CO. Reaction of CO, consuming oxygen from the chemisorption and oxide phases, led to formation of CO_2, which instantaneously desorbed from the surface and was detected in the gas phase via quadrupole mass spectrometry (QMS; see e.g. Refs. [34,35]).

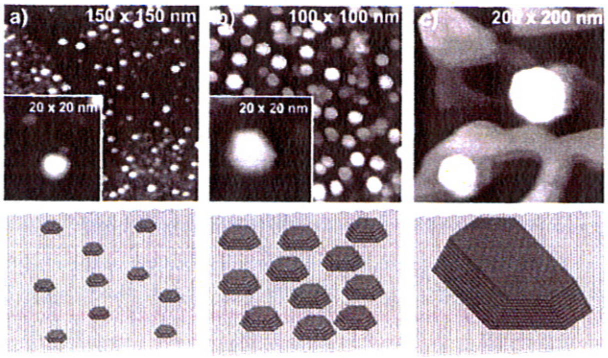

Figure 2. STM images and schematic representations of the model catalyst surface for different metal loadings after stabilization by oxidation and reduction cycles; nominal Pd thickness: a) 0.3 Å (average particle size 3 nm); b) 4.0 Å Pd (particle size 7 nm); c) 15 Å Pd (particle size ≈65 nm).

The pulsed MB titration experiment was described previously.[20] It allows an exact quantification of the oxygen release and provides detailed insights into the related reduction kinetics. A typical example of a pulsed MB titration is shown in Figure 1b. The most important point to note is that the CO_2 signal reveals the presence of two reaction channels. During the first CO pulse, very fast CO_2 formation is observed. This fast reaction channel was previously attributed to the reaction of chemisorbed atomic oxygen on metallic Pd with CO. After a single CO pulse, however, the reservoir of chemisorbed O is depleted, and the following slower CO_2 formation involves oxygen that originates from Pd oxide. In a previous study[20] it was shown that this Pd oxide is formed preferentially at the Pd/Fe_3O_4 interface and not at the outer surface of the Pd particles. As a result, a large fraction of the outer particle surface remains metallic for particles of intermediate size (4–10 nm). Reduction of the Pd oxide phase proceeds by means of slow decomposition and release of oxygen onto the metallic part of the surface, followed by rapid reaction with adsorbed CO. Decomposition of the interface oxide is, in general, the rate-controlling step under the present experimental conditions. It limits the rate of oxygen release and CO_2 formation which is typically spread over up to 100 CO pulses. It should be pointed out that the oxidation and reduction process is fully reversible and can be repeated many times without significant decrease in the oxygen uptake.

The total amount of oxygen released from the system can be determined easily by integrating the CO_2 formation over all CO pulses. The corresponding result for 7-nm particles is shown in the inset in Figure 1. We found that the amount of oxygen stored in the Pd interface oxide layer by far exceeds the amount of oxygen that could be chemisorbed on a purely metallic Pd particle. For the 7-nm particles, for instance, the oxygen release is approximately four times greater than expected for pure chemisorption. These quantitative measurements of oxygen release by means of MB titration experiments were confirmed by measurements of the oxygen uptake by pulsed sticking coefficient measurements.[36] In the same study, it was shown by isotopic exchange experiments that oxidation and reduction of the Fe_3O_4 support does not contribute significantly to the oxygen uptake and release. Also, it was shown by photoelectron spectroscopy (PES) that the particles are fully reduced by extended CO exposure.

In the next step we considered the size dependence of the Pd particle oxidation. For an interface-controlled oxidation mechanism, we would expect a strong size dependence, because the accessibility of the particle/support interface is expected to decrease with increasing size. In order to experimentally verify this hypothesis, we systematically measured the oxygen release by means of pulsed MB titration experiments over a broad range of particle sizes from about 2 to 100 nm. The corresponding structural and morphological properties were extracted from STM (see Figure 2 and the Supporting Information).

To identify the role of particle-size-dependent Pd oxidation in the oxygen uptake and release process, we first estimated the amount of oxygen release that would be expected if there was no Pd oxide formation at all, but pure oxygen chemisorption on metallic Pd only. For this purpose, we determined the Pd surface area available for chemisorption per unit area of the Fe_3O_4 support by means of CO sticking coefficient measurements. The CO adsorption was converted into a hypothetical O uptake assuming O chemisorption only (for details see the Supporting Information). The result is shown in Figure 3a (blue curve): We found that initially the Pd surface area increases monotonically with increasing Pd loading or particle size, whereas for high Pd loadings or large particle sizes the Pd surface area is nearly constant. The reason is that for low loading (small particles) the island density changes only weakly, whereas the particle size increases with metal loading. At high loading (large particles), however, the particle density decreases rapidly due to coalescence. Increasing particle size and decreasing particle density nearly compensate, resulting in an almost constant Pd surface area. It should be noted that the measurements of the Pd surface area by means of the CO sticking coefficient are in full accordance with estimates derived from STM data.

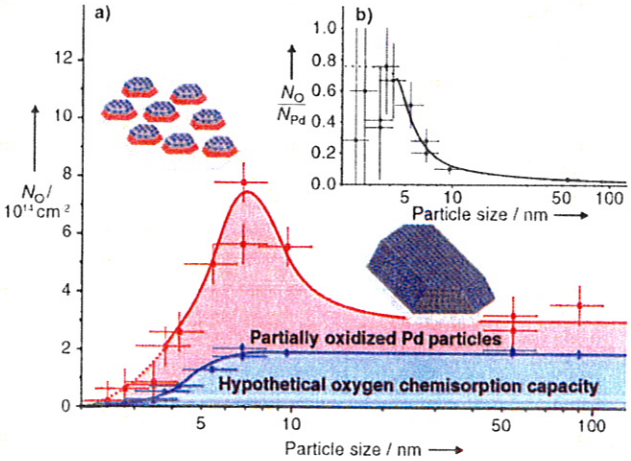

Figure 3. Oxygen storage on a Pd/Fe_3O_4 model catalyst after 100 s (≈130 L) oxygen exposure at 500 K as a function of Pd particle size: a) Hypothetical oxygen release assuming regular chemisorption on metallic Pd particles only and no oxidation (blue curve) and experimentally determined oxygen release on partially oxidized Pd particles (red curve); b) mean stoichiometry of the Pd particles after oxygen treatment.

In a second step, the actual oxygen-storage capacity was quantified by pulsed MB titration experiments (see Figure 3, red curve). We found that the experimentally determined oxygen release is completely different from that expected assuming chemisorption only: First, the release was significantly larger than expected for pure chemisorption. Secondly, a pronounced maximum of the total oxygen release was found for particle sizes around 7 nm.

The differences between the experimental oxygen release on the one hand and the hypothetical oxygen-chemisorption capacity on the other are attributed to the partial oxidation of the Pd particles. It is apparent that the contribution due to Pd oxide formation shows a pronounced size dependence. To obtain some additional information on the oxidation process, we calculated the total stoichiometry of the particles after oxygen treatment (see Figure 3b, calculated by dividing the total oxygen release by the total Pd loading). The result shows that the average Pd oxidation state monotonically decreases with increasing particle size: Whereas in the limit of small particles (< 3 nm) the stoichiometry corresponds to almost PdO, the oxygen/Pd ratio decreases to approximately $PdO_{0.25}$ at sizes around 7 nm and, finally, to $PdO_{<0.05}$ for the largest particles investigated. (Note that these values represent an average over metallic parts of the three-dimensional particles with chemisorbed oxygen and oxidized parts).

From this observation the following scenario can be derived: As shown in our previous work, oxidation of the Pd particles proceeds by initial chemisorption of oxygen on the metallic Pd particles and successive conversion of this chemisorbed oxygen to Pd oxide layers, preferentially at the particle/support interface.[20,36] For sufficiently small particles, no stable metal nucleus remains after formation of the interface oxide, resulting in complete oxidation of the nanoparticle (stoichiometry PdO). It is noteworthy that in a theoretical study Huber et al. recently showed that the interaction with the oxide support may lead to a significant stabilization of very small oxidized Pd clusters.[37] For larger particles (> 3 nm), however, oxidation is not complete and a metallic cap remains on top of the Pd interface oxide. It may be expected that for particles of this size interface, oxidation requires ion transport from the particle boundary along the metal/oxide interface. As shown experimentally, oxide formation and decomposition are rather slow processes, even for particles of intermediate size (around 7 nm). Thus, we may anticipate that with increasing particle size, interface transport finally becomes too slow to facilitate complete interface oxidation. As a result, oxygen storage by oxide formation at the Pd interface becomes kinetically hindered in the large particle limit (10–100 nm).

It is noteworthy that the hindrance of Pd oxide formed on large particles is directly reflected in the MB titration experiment. In Figure 4 a direct comparison of the CO_2 signal during the first few pulses of a MB titration experiment is shown for two samples corresponding to small (4 nm) and large (90 nm) particles. The CO_2 signal during the first CO pulse, which reflects the amount of chemisorbed oxygen on the metallic Pd surface, was significantly higher in case of the

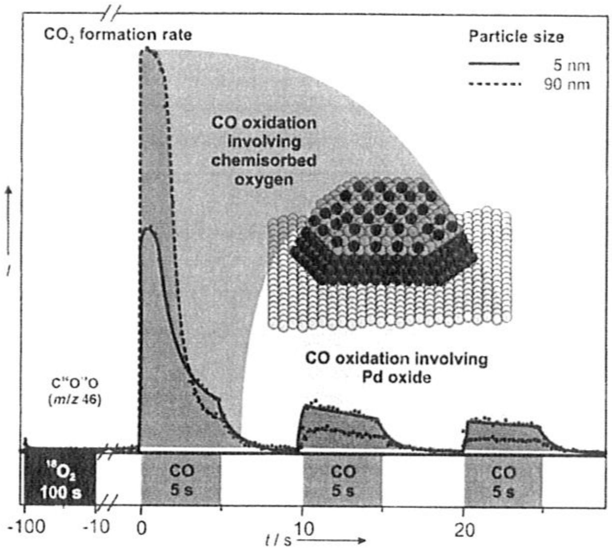

Figure 4. CO_2 formation rate during the first CO pulses of a CO titration experiment on preoxidized Pd/Fe_3O_4 model catalysts with different particles sizes.

large particles. In contrast, the CO_2 formation rate involving Pd oxide, which is represented by the following CO pulses, was less intense for the large particles further substantiating the strongly decreased oxide formation. (It should be noted that even on the largest particles a minor amount of oxide formation is detected. This remaining oxide formation may originate from particle sites that are more susceptible for oxidation such as (100) facets, steps, or defects and from remaining oxide formation at the particle boundaries; see Refs. [11–14] for a discussion of the interaction of Pd(111) and Pd(100) with oxygen.)

In summary we have shown that the interface-controlled oxidation mechanism for Pd nanoparticles supported on an Fe_3O_4 film gives rise to a pronounced particle-size dependence of the oxidation and reduction behavior: In the limit of small particles (< 3 nm) complete oxidation to PdO occurs easily, whereas in the range of intermediate particle sizes (4–10 nm) only partial oxidation takes place, primarily at the metal/support interface. For larger particles (approximately 10–100 nm) the formation of the Pd interface oxide is kinetically hindered, presumably as a result of slow ion transport along the particle/support interface.

The formation of the interface oxide is fully reversible and allows uptake and release of much larger quantities of oxygen than would be expected for pure chemisorption on Pd metal. The size-dependent oxidation behavior has major implications for the oxygen-storage mechanism. In particular, it gives rise to a pronounced maximum of the oxygen-uptake capacity per unit of support surface area as a function of the metal loading. For low metal loading and small particles, oxidation is highly efficient, but the total oxygen-storage capacity is limited by the small amount of Pd available per catalyst surface area. (It should be noted that the oxygen-storage capacity cannot be increased by increasing the particle density because of oxygen-induced sintering effects at elevated temperatures, see Ref. [33]). For high metal loading and large particles, the amount of Pd available per support surface area is large, but the formation of Pd oxide becomes kinetically hindered. The maximum oxygen uptake is observed at intermediate Pd loading: Here, the particles are large enough to allow substantial amounts of interface oxide to be formed but are yet small enough to avoid strong kinetic hindrance to oxide formation.

The oxygen-storage mechanism and its size dependence are expected to play an important role in the kinetics of oxidation reactions on the present model system, especially under non-steady-state conditions. It might be anticipated that similar effects can be observed for other supported particle systems as well. Thus, it is likely that particle-size-dependent oxidation and reduction phenomena will have to be considered in the development of realistic microkinetic descriptions of catalytic reactions.

[1] *Handbook of Heterogeneous Catalysis* (Eds.: G. Ertl, H. Knoezinger, J. Weitkamp), VCH, Weinheim, **1997**.

[2] J. M. Thomas, W. J. Thomas, *Principle and Practice of Heterogeneous Catalysis*, VCH, Weinheim, **1997**.

[3] H. Conrad, G. Ertl, J. Küppers, E. E. Latta, *Surf. Sci.* **1977**, *65*, 235.

[4] R. Imbihl, J. E. Demuth, *Surf. Sci.* **1986**, *173*, 395.

[5] S.-L. Chang, P. A. Thiel, *J. Chem. Phys.* **1988**, *88*, 2071.

[6] X. Guo, A. Hoffman, J. T. Yates, Jr., *J. Chem. Phys.* **1989**, *90*, 5787.

[7] V. A. Bondzie, P. Kleban, D. J. Dwyer, *Surf. Sci.* **1996**, *347*, 319.

[8] E. H. Voogt, A. J. M. Mens, O. L. J. Gijzeman, J. W. Geus, *Surf. Sci.* **1997**, *373*, 210.

[9] F. P. Leisenberger, G. Koller, M. Sock, S. Surnev, M. G. Ramsey, F. P. Netzer, B. Klötzer, K. Hayek, *Surf. Sci.* **2000**, *445*, 380.

[10] V. A. Bondzie, P. H. Kleban, D. J. Dwyer, *Surf. Sci.* **2000**, *465*, 266.

[11] G. Zheng, E. I. Altman, *Surf. Sci.* **2000**, *462*, 151.

[12] G. Zheng, E. I. Altman, *Surf. Sci.* **2002**, *504*, 253.

[13] E. Lundgren, G. Kresse, C. Klein, M. Borg, J. N. Andersen, M. De Santis, Y. Gauthier, C. Konvicka, M. Schmid, P. Varga, *Phys. Rev. Lett.* **2002**, *88*, 246103.

[14] M. Todorova, E. Lundgren, V. Blum, A. Mikkelsen, S. Gray, J. Gustafson, M. Borg, J. Rogal, K. Reuter, J. N. Andersen, M. Scheffler, *Surf. Sci.* **2003**, *541*, 101.

[15] E. Lundgren, J. Gustafson, A. Mikkelsen, J. N. Andersen, A. Stierle, H. Dosch, M. Todorova, J. Rogal, K. Reuter, M. Scheffler, *Phys. Rev. Lett.* **2004**, *92*, 046101.

[16] M. Todorova, K. Reuter, M. Scheffler, *Phys. Rev. B* **2005**, *71*, 195403.

[17] H. Over, Y. D. Kim, A. P. Seitsonen, S. Wendt, E. Lundgren, M. Schmid, P. Varga, A. Morgante, G. Ertl, *Science* **2000**, *287*, 1474.

[18] G. Zheng, E. I. Altmann, *J. Phys. Chem. B* **2002**, *106*, 1048.

[19] B. L. M. Hendriksen, S. C. Bobaru, J. W. M. Frenken, *Surf. Sci.* **2004**, *552*, 229.

[20] T. Schalow, M. Laurin, B. Brandt, S. Schauermann, S. Guimond, H. Kuhlenbeck, D. E. Starr, S. K. Shaikhutdinov, J. Libuda, H.-J. Freund, *Angew. Chem.* **2005**, *117*, 7773; *Angew. Chem. Int. Ed.* **2005**, *44*, 7601.

[21] C. R. Henry, *Surf. Sci. Rep.* **1998**, *31*, 231.
[22] V. P. Zhdanov, B. Kasemo, *Surf. Sci. Rep.* **2000**, *39*, 25.
[23] T. P. St. Clair, D. W. Goodman, *Top. Catal.* **2000**, *13*, 5.
[24] H.-J. Freund, M. Bäumer, J. Libuda, T. Risse, G. Rupprechter, S. Shaikhutdinov, *J. Catal.* **2003**, *216*, 223.
[25] J. Libuda, H.-J. Freund, *Surf. Sci. Rep.* **2005**, *57*, 157.
[26] G. Scoles, *Atomic and Molecular Beam Methods*, Oxford University Press, Oxford, **1988**.
[27] M. P. D'Evelyn, R. J. Madix, *Surf. Sci. Rep.* **1984**, *3*, 413.
[28] C. T. Rettner, D. J. Auerbach, J. C. Tully, A. W. Kleyn, *J. Phys. Chem.* **1996**, *100*, 13021.
[29] A. W. Kleyn, *Chem. Soc. Rev.* **2003**, *32*, 87.
[30] W. Weiss, W. Ranke, *Prog. Surf. Sci.* **2002**, *70*, 1.
[31] C. Lemire, R. Meyer, V. Henrich, S. K. Shaikhutdinov, H.-J. Freund, *Surf. Sci.* **2004**, *572*, 103.
[32] R. Meyer, S. K. Shaikhutdinov, H.-J. Freund, *Z. Phys. Chem.* **2004**, *218*, 905.
[33] T. Schalow, B. Brandt, D. E. Starr, M. Laurin, S. Schauermann, S. K. Shaikhutdinov, J. Libuda, H.-J. Freund, *Catal. Lett.* **2006**, *107*, 189.
[34] T. Engel, G. Ertl, *J. Chem. Phys.* **1978**, *69*, 1267.
[35] T. Engel, G. Ertl, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, Vol. 4* (Eds.: D. A. King, D. P. Woodruff), Elsevier, Amsterdam, **1982**, p. 73.
[36] T. Schalow, B. Brandt, S. Schauermann, J. Libuda, H.-J. Freund, unpublished results.
[37] B. Huber, P. Koskinen, H. Häkkinen, M. Moseler, *Nat. Mater.* **2006**, *5*, 44.