

Catalytic activity of Au nanoparticles

Au is usually viewed as an inert metal, but surprisingly it has been found that Au nanoparticles less than 3–5 nm in diameter are catalytically active for several chemical reactions. We discuss the origin of this effect, focusing on the way in which the chemical activity of Au may change with particle size. We find that the fraction of low-coordinated Au atoms scales approximately with the catalytic activity, suggesting that atoms on the corners and edges of Au nanoparticles are the active sites. This effect is explained using density functional calculations.

Britt Hvolbæk¹, Ton V. W. Janssens², Bjerne S. Clausen², Hanne Falsig³, Claus H. Christensen³, and Jens K. Nørskov^{1*}

¹Center for Atomic-scale Materials Design, Department of Physics, NanoDTU, Technical University of Denmark, DK-2800 Lyngby, Denmark

²Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

³Center for Sustainable and Green chemistry, Department of Chemistry, NanoDTU, Technical University of Denmark, DK-2800 Lyngby, Denmark.

*E-mail: norskov@fysik.dtu.dk

Catalysts are widely used in the large-scale manufacture of chemicals and in the production of fine chemicals and pharmaceuticals. Fuel processing is a good example: the gasoline that we use in our cars requires at least ten different catalysts during its transformation from crude oil. Environmental technologies also rely heavily on catalysts; the best known example being the catalytic converter in the exhaust of every car. It is estimated that more than 20% of the gross national product (GNP) of industrial countries relies in one way or another on catalysis¹.

In heterogeneous catalysis, the reacting molecules adsorb on the catalytically active solid surface. Chemical bonds are broken and formed on the surface and eventually the products are released back into the liquid or gas phase. Many of the heterogeneous catalysts used in industry today consist of small particles of a catalytically

active material, typically with a diameter of 1–10 nm, anchored on a porous support. The use of nanoparticles results in a large contact area between the active material of the catalyst and the surrounding gas or liquid phase. This ensures that the catalytic material is used effectively. One of the interesting scientific and technological challenges associated with the use of nanoparticles as catalysts is the understanding of how the composition and atomic-scale structure of nanoparticles produce the best catalytic activity. The second challenge is to synthesize these particles with maximum control over the composition and structure. Modern nanotechnology methods clearly offer great potential for future developments in both characterization and synthesis of heterogeneous catalysts based on supported nanoparticles.

Maximizing the surface area is not the only reason for using nanoparticles as heterogeneous catalysts. Au is usually considered

chemically inert²⁻⁴, but in 1987 Haruta *et al.*⁵ showed that nanosized (<5 nm) Au particles can be very effective catalysts. This indicates that the catalytic properties of a particular material can be dramatically influenced by the particle size. The fact that Au particles with diameters of about 5 nm or less have unique catalytic properties has initiated a search both for an explanation of this quite unexpected effect and for chemical reactions that are catalyzed by Au⁵⁻³⁴. In some cases, catalysts based on nanosized Au particles allow a significantly lower reaction temperature than used in existing processes, which is promising for the development of energy efficient processes³⁵⁻³⁸.

Here we discuss some of the reasons why small Au particles are catalytically active. Several explanations for the catalytic activity of such particles have been proposed, including quantum size effects^{10,11,39-41}, charge transfer to and from the support⁴²⁻⁴⁴ or support-induced strain⁴⁵, oxygen spill-over to and from the support^{12,46-55}, the Au oxidation state^{27,56-72}, and the role of very low-coordinated Au atoms in nanoparticles^{34,38,45,73-84}. It is likely that several of the aforementioned effects occur simultaneously. In this review, we concentrate on some of the effects that are associated with the particle size alone. These will always be present, independent of the support material.

The reactivity of Au and Au nanoparticles

The ability of a metal surface to form bonds with a gas is a measure of how noble it is. The nobility of a metal is well illustrated by the ability of the surface of the metal to oxidize, that is, to chemisorb oxygen dissociatively. Fig. 1 shows calculated oxygen chemisorption energies on a selection of transition metals⁸⁵. It can be seen that the metals located above and to the left of Au in the periodic table have increasingly large chemisorption energies, and that the metals neighboring Au bind oxygen weakly. Au is the only metal with an

Cr	Mn	Fe	Co	Ni	Cu
		-6,30	-5,07	-3,90	-2,51
Mo	Tc	Ru	Rh	Pd	Ag
-7,48		-4,62	-4,03	-1,20	-0,65
W	Re	Os	Ir	Pt	Au
-8,62			-4,65	-2,17	+0,54

Fig. 1 The dissociative chemisorption energies for oxygen on transition metal surfaces with respect to a molecule in vacuum calculated by density functional theory (DFT). All results are for adsorption at either a body-centered cubic (210) surface (for Fe, Mo, W) or a face-centered cubic (211) surface (other metals)⁸⁵.

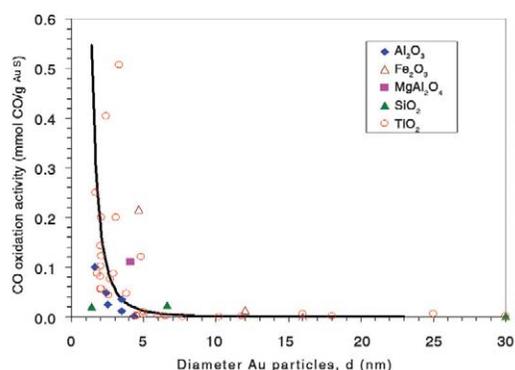


Fig. 2 Reported catalytic activities (in $\text{mmol/g}_{\text{Au}} \text{ s}$, left axis) for CO oxidation at 273 K as a function of Au particle size (d , in nanometers) for different support materials^{14,23,53,55,80,83,88-94}. The supports are indicated by the symbol shape: open symbols correspond to reducible supports, closed symbols to irreducible supports. The solid curve shows the calculated fraction of atoms located at the corners of nanoparticles as a function of particle diameter for uniform particles shaped as the top half of a regular cuboctahedron (see also Fig. 5). (Adapted from^{34,80}.)

endothermic chemisorption energy, which implies that it does not bind oxygen at all. This illustrates the well-known fact that Au is inert in an oxygen atmosphere⁸⁶.

The trends in Fig. 1 can be understood by considering the chemical bond that forms as a result of the coupling of the oxygen valence states and the metal d -states in the so-called d -band model^{4,87}. Au has d -states so low in energy that the interaction with oxygen $2p$ -states is net repulsive. It is therefore unlikely that Au should be a good catalyst for an oxidation reaction. Nevertheless, the oxidation of CO (as it takes place over Pt-based catalysts in an automotive exhaust system) is one of the reactions where Au nanoparticles are a very good catalyst, even at room temperature. This is illustrated in Fig. 2, which is a compilation of experimental data of the CO oxidation activity as a function of the size of Au nanoparticle catalysts with different support materials^{14,23,53,55,80,83,88-94}. It is clear that the activity is strongly dependent on the size of the Au nanoparticles, and that only catalysts with Au particles below 5 nm show catalytic activity. Furthermore, it can also be seen that the activity varies depending on the support. These effects are clearly important, but the results of Fig. 2 indicate that the most important effect is that of size. In this review, therefore, we concentrate on the intrinsic catalytic activity of Au particles bearing in mind that there are additional effects to consider in order to develop a complete picture of Au catalysis.

Density functional theory simulations

To investigate why the size of Au nanoparticles has such a significant influence on the catalytic activity, we apply density functional theory calculations (DFT) to simulate the behavior of adsorbed molecules on a Au nanoparticle. Rather than simulating a Au cluster of 3–5 nm with thousands of atoms, we simulate a ten atom cluster (as shown in the insert in Fig. 3). We do not include a substrate in the simulations either,

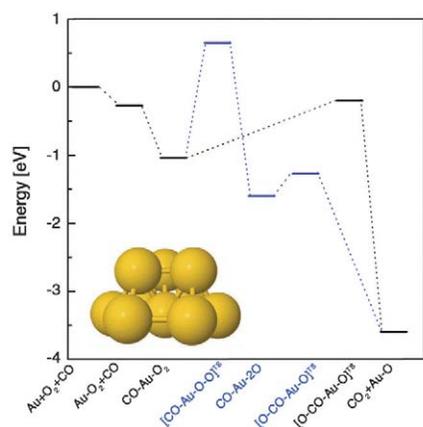


Fig. 3 Calculated reaction energies for CO oxidation on an Au₁₀ cluster (shown in insert). The lower layer of the cluster is kept fixed in the direction perpendicular to the support. Two reaction routes are shown: one dissociates O₂ before reaction with CO to form CO₂, and the other reacts molecular O₂ directly with CO.

so the results originate only from the Au nanoparticles themselves. This is clearly an oversimplification of a real catalytic system, but is adequate to illustrate the effect of the particle size qualitatively. We consider below the CO oxidation as a test reaction.

The calculated energy diagram of two possible routes of CO oxidation is shown in Fig. 3^{34,75}. One route dissociates O₂ before reacting with CO to form CO₂; the other is a reaction between molecular O₂ and CO. The results indicate that CO oxidation is possible at room temperature. It can be seen that the reaction between molecular O₂ and CO is favored – it requires considerably lower activation energy than the reactions involving dissociation of O₂⁴⁸. The single adsorbed O-atom left over from the reaction between O₂ and CO will react with another CO following the last half of the other route.

The energy diagram also reveals what could be an important clue to understanding the ability of Au nanoparticles to act as a catalyst: both O₂, O, and CO bind to the surface of the cluster. This is in sharp contrast to extended Au surfaces (see, for example, Fig. 1). It turns out that a useful way of characterizing the difference between Au nanoparticles and extended Au surfaces is by considering the metal coordination number of the Au atoms to which the reactants (O₂, O, or CO) bond (Fig. 4). Au atoms on a close-packed surface have nine Au neighbors, at steps on the surface the coordination number is seven, but at the corners of a small particle it can be as low as three to four. Fig. 4 shows that the binding energy decreases approximately linearly with decreasing coordination number^{34,80}.

Small particles have a relatively large number of low-coordinated Au atoms, which are located at the edges and, in particular, at the corners of particles. The simple analysis above indicates that these Au atoms are able to bind CO and oxygen, which is a prerequisite for a catalytic reaction. It is therefore conceivable that at these sites the CO oxidation reaction is possible at room temperature – the barriers are

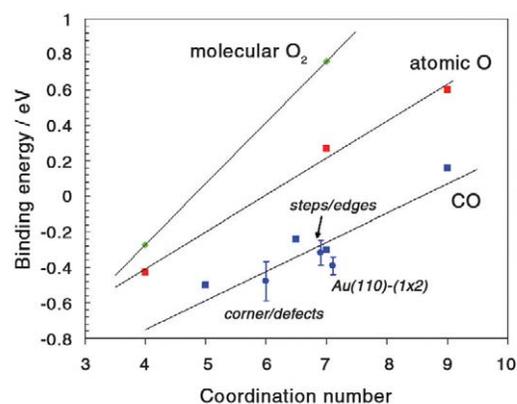


Fig. 4 The correlation between the binding energies for O₂, O, and CO on Au and the coordination number of the Au atoms in different surfaces and clusters. The binding energies are calculated using DFT and the experimental values are from elsewhere^{34,102}. The superscript TS denotes the transition state of the reaction.

small and, importantly, the intermediates and CO₂ that are formed are only weakly bound, so it is not necessary to have a high temperature to keep parts of the surface free.

If the low-coordinated corner sites are the active sites, then the catalytic activity should scale with the number of low-coordinated atoms in the nanoparticles, and not with the surface area. Fig. 5 shows a calculation of the fraction of atoms that are located at either corners, edges, or on surfaces in the top half of a truncated octahedron as a function of the particle diameter³⁴. Clearly, the total number of surface atoms changes only slightly when the particle size decreases from 10 nm to 2 nm. However, the fraction of corners increases significantly when the particle size is less than 4 nm and scales approximately as d^{-3} as the diameter of the particles shrinks. The increase in the estimated fraction of corner atoms behavior coincides with a generally observed increase in CO oxidation activity with decreasing Au particle size

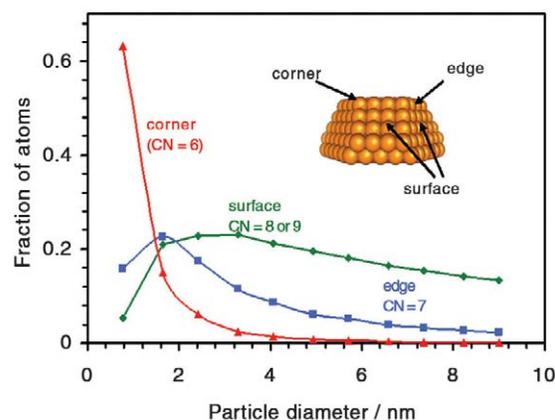


Fig. 5 Calculated fractions of Au atoms at corners (red), edges (blue), and crystal faces (green) in uniform nanoparticles consisting of the top half of a truncated octahedron as a function of Au particle diameter. The insert shows a truncated octahedron and the position of representative corner, edge, and surface atoms. (Reproduced with permission from³⁴. © 2007 Springer.)

(Fig. 2). This supports the hypothesis that the total number of atoms located at the corners of the nanoparticles has a major influence on the activity of a supported Au catalyst.

Experimental observations

The simulation results showing that chemisorption strength increases with decreasing coordination number is supported by a number of recent experiments. Temperature-programmed desorption (TPD) of CO on well-defined surfaces of Au and Au particles shows that the desorption temperature increases with decreasing coordination number^{34,77,95–97}. This indicates that the chemisorption becomes stronger, in agreement with simulations. In fact, the estimated chemisorption energies are close to the values expected from calculations, as indicated in Fig. 4.

Experiments show that low-coordinated sites on a densely packed Au(111) surface produced by ion bombardment are also active for CO oxidation⁹⁸. Recently, Xu *et al.*⁹⁹ have shown that unsupported nanoporous Au is an active catalyst for CO oxidation. The nanoporous Au catalyst, with pore sizes of less than 6 nm, is produced by etching away Ag from an Ag/Au alloy. The results provide additional support for the hypothesis that metallic Au is intrinsically catalytically active if the coordination number of the Au atoms is sufficiently low.

Evidence for the scaling of the catalytic activity of Au nanoparticles with the number of corner atoms has been provided by Overbury *et al.*⁹³. They evaluated the dimensionality of the dominating active site by correlating the CO oxidation activity of a Au/TiO₂ catalyst with Au particle size by combining extended X-ray absorption fine structure (EXAFS) with *in situ* activity measurements. The particle size is varied by heating samples of the catalyst to different temperatures. This is done to eliminate possible variations in the preparation of different batches of catalyst. Fig. 6 shows the correlation for 4.5 wt.% and 7.2 wt.% Au at 273 K. The slope of the lines through the data is -2.1 and -2.8 , respectively. This indicates that the corners (slope: -3) and to a lesser extent edge sites (slope: -2) are the dominating site for 7.2 wt.% whereas edges and to a lesser extent corners contribute to the active site for 4.5 wt.%.

In studies by Janssens *et al.*^{34,83,100}, a geometric model for Au particles on TiO₂, MgAl₂O₄, and Al₂O₃ supports was constructed based on scanning transmission electron microscopy (STEM) and EXAFS measurements. This allows an accurate count of the corner atoms in these supported catalysts. By comparing their catalytic activities, it has been found that the turn over frequency per corner atom for Au/TiO₂ and Au/MgAl₂O₄ catalysts is the same, and any difference in catalytic activity between these two materials can therefore be entirely ascribed to differences in particle size and shape, which determine the total number of low-coordinated corner atoms. The turn over frequency per corner atom for Au/Al₂O₃ is about a factor of four lower, which indicates an additional support effect in this case. This example nicely illustrates that the catalytic activity of Au nanoparticles is not

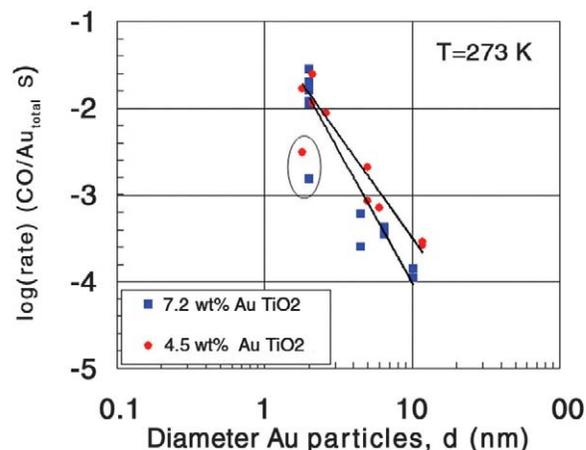


Fig. 6 Activity at 273 K as a function of Au particle diameter for two series of Au/TiO₂ catalysts containing 4.5 wt.% and 7.2 wt.% Au, respectively. The particle size has been varied by heat treatment at various temperatures between 423 K and 773 K. The rate is expressed per total amount of Au. Best power law fits to the data (excluding the two encircled points) are shown for each catalyst. (Reproduced with permission from⁹³. © 2006 Elsevier.)

the result of a single contribution, but the result of a combination of different effects.

Conclusions

Nanoscale effects are found throughout heterogeneous catalysis, but are perhaps best illustrated by the remarkable catalytic activity of Au nanoparticles. We still do not understand in detail the many effects that contribute to this activity, but in this review we have pointed to one very important effect: the increased reactivity of low-coordinated Au atoms. Such atoms are particularly abundant on the smallest nanometer-sized nanoparticles, and this may go a long way toward explaining the catalytic activity of such Au nanoparticles.

We are far from having explored all the possible applications of Au catalysis, but the system is extremely interesting. One intriguing property of Au nanoparticle catalysts is that they can catalyze several reactions at or even below room temperature. This could give energy savings in many catalytic processes, and provides an interesting analogue to enzyme catalysis, which can also take place at room temperature.

We also need to be able to synthesize Au nanoparticles in forms that are stable over long time periods. Understanding the interaction between Au particles and their support material is a key issue¹⁰¹. Finally, the question arises as to whether there are other classes of catalytic materials where nanoscale effects are as pronounced as for Au. We clearly need more insight. **nt**

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REFERENCES

1. Maxwell, I., *Stud. Surf. Sci. Catal.* (1996) **101**, 1
2. Wickham, D. T., et al., *Prepr. – Am. Chem. Soc., Div. Pet. Chem.* (1992) **37**, 1034
3. Lazaga, M. A. A., et al., *Catalytic selective oxidation. ACS Symposium Series* (1993) **523**, 90
4. Hammer, B., and Nørskov, J. K., *Nature* (1995) **376**, 238
5. Haruta, M., et al., *Chem. Lett.* (1987) **16**, 405
6. Kobayashi, T., et al., *Sens. Actuators* (1988) **13**, 339
7. Haruta, M., et al., *J. Catal.* (1989) **115**, 301
8. Haruta, M., et al., *Stud. Surf. Sci. Catal.* (1989) **44**, 33
9. Haruta, M., et al., *J. Catal.* (1993) **144**, 175
10. Valden, M., et al., *Science* (1998) **281**, 1647
11. Valden, M., et al., *Catal. Lett.* (1998) **56**, 7
12. Bond, G. C., and Thomson, D. T., *Catal. Rev. – Sci. Eng.* (1999) **41**, 319
13. Hayashi, T., et al., *Prepr. – Am. Chem. Soc., Div. Pet. Chem.* (1996) **41**, 71
14. Haruta, M., *Stud. Surf. Sci. Catal.* (1997) **110**, 123
15. Dekkers, M. A. P., et al., *Catal. Today* (1999) **54**, 381
16. Kalvachev, Y. A., et al., *J. Catal.* (1999) **186**, 228
17. Uphade, B. S., et al., *Appl. Catal. A* (2000) **190**, 43
18. Grisel, R. J. H., and Nieuwenhuys, B. E., *Catal. Today* (2001) **64**, 69
19. Grisel, R. J. H., et al., *Top. Catal.* (2001) **16/17**, 425
20. Carrettin, S., et al., *Chem. Commun.* (2002), 696
21. Choudhary, T. V., and Goodman, D. W., *Top. Catal.* (2002) **21**, 25
22. Landon, P., et al., *Chem. Commun.* (2002), 2058
23. Schimpf, S., et al., *Catal. Today* (2002) **72**, 63
24. Carrettin, S., et al., *Phys. Chem. Chem. Phys.* (2003) **5**, 1329
25. Gluhoi, A. C., et al., *J. Catal.* (2003) **219**, 197
26. Okumura, M., et al., *Chem. Lett.* (2003) **32**, 822
27. Carrettin, S., et al., *Top. Catal.* (2004) **27**, 131
28. Meyer, R., et al., *Gold Bull.* (2004) **37**, 72
29. Abad, A., et al., *Angew. Chem. Int. Ed.* (2005) **44**, 4066
30. Gluhoi, A. C., et al., *J. Catal.* (2005) **229**, 154
31. Gluhoi, A. C., et al., *J. Catal.* (2005) **232**, 96
32. Hughes, M. D., et al., *Nature* (2005) **437**, 1132
33. Nijhuis, T. A., et al., *Ind. Eng. Chem. Res.* (2006) **45**, 3447
34. Janssens, T. V. W., et al., *Top. Catal.* (2007) **44**, 15
35. Kim, D. H., et al., *Catal. Lett.* (2004) **98**, 11
36. Lin, S. D., et al., *Catal. Today* (2004) **90**, 3
37. Christensen, C. H., et al., *Angew. Chem. Int. Ed.* (2006) **45**, 4648
38. Burch, R., *Phys. Chem. Chem. Phys.* (2006) **8**, 5483
39. Lai, X., et al., *Prog. Surf. Sci.* (1998) **59**, 25
40. Lai, X., et al., *J. Mol. Catal. A* (2000) **162**, 33
41. Yang, Z., et al., *Phys. Rev. B* (2000) **61**, 14066
42. Sanchez, A., et al., *J. Phys. Chem. A* (1999) **103**, 9573
43. Ricci, D., et al., *Phys. Rev. Lett.* (2006) **97**, 036106
44. van Bokhoven, J. A., et al., *Angew. Chem. Int. Ed.* (2006) **45**, 4651
45. Mavrikakis, M., et al., *Catal. Lett.* (2000) **64**, 101
46. Hammer, B., *Top. Catal.* (2006) **37**, 3
47. Liu, L. M., et al., *J. Am. Chem. Soc.* (2006) **128**, 4017
48. Liu, Z.-P., et al., *J. Am. Chem. Soc.* (2002) **124**, 14770
49. Molina, L. M., and Hammer, B., *Phys. Rev. Lett.* (2003) **90**, 206102
50. Molina, L. M., et al., *J. Chem. Phys.* (2004) **120**, 7673
51. Molina, L. M., and Hammer, B., *Phys. Rev. B* (2004) **69**, 155424
52. Molina, L. M., and Hammer, B., *Appl. Catal. A* (2005) **291**, 21
53. Okumura, M., et al., *Catal. Lett.* (1998) **51**, 53
54. Sakurai, H., et al., *Appl. Catal. A* (2005) **291**, 179
55. Schubert, M. M., et al., *J. Catal.* (2001) **197**, 113
56. Finch, R. M., et al., *Phys. Chem. Chem. Phys.* (1999) **1**, 485
57. Hao, Z., et al., *React. Kinet. Catal. Lett.* (2000) **70**, 153
58. Bera, P., and Hegde, M. S., *Catal. Lett.* (2002) **79**, 75
59. Hodge, N. A., et al., *Catal. Today* (2002) **72**, 133
60. Kung, H. H., et al., *J. Catal.* (2003) **216**, 425
61. Carrettin, S., et al., *Angew. Chem. Int. Ed.* (2004) **43**, 2538
62. Costello, C. K., et al., *J. Phys. Chem. B* (2004) **108**, 12529
63. Fierro-Gonzalez, J. C., and Gates, B. C., *J. Phys. Chem. B* (2004) **108**, 16999
64. Guzman, J., and Gates, B. C., *J. Am. Chem. Soc.* (2004) **126**, 2672
65. Carrettin, S., et al., *Appl. Catal. A* (2005) **291**, 247
66. Fierro-Gonzalez, J. C., et al., *Catal. Lett.* (2005) **101**, 265
67. Fu, L., et al., *J. Phys. Chem. B* (2005) **109**, 3704
68. Chrétien, S., and Metiu, H., *Catal. Lett.* (2006) **107**, 143
69. Comas-Vives, A., et al., *J. Am. Chem. Soc.* (2006) **128**, 4756
70. Concepción, P., et al., *Appl. Catal. A* (2006) **307**, 42
71. González-Arellano, C., et al., *J. Catal.* (2006) **238**, 497
72. Hutchings, G. J., et al., *J. Catal.* (2006) **242**, 71
73. Grunwaldt, J.-D., et al., *J. Catal.* (1999) **186**, 458
74. Lopez, N., and Nørskov, J. K., *Surf. Sci.* (2002) **515**, 175
75. Lopez, N., and Nørskov, J. K., *J. Am. Chem. Soc.* (2002) **124**, 11262
76. Mills, G., et al., *J. Chem. Phys.* (2003) **118**, 4198
77. Shaikhutdinov, Sh. K., et al., *Catal. Lett.* (2003) **86**, 211
78. Lemire, C., et al., *Surf. Sci.* (2004) **552**, 27
79. Lemire, C., et al., *Angew. Chem. Int. Ed.* (2004) **43**, 118
80. Lopez, N., et al., *J. Catal.* (2004) **223**, 232
81. Biener, M. M., et al., *Surf. Sci.* (2005) **590**, L259
82. Deng, X., et al. *J. Am. Chem. Soc.* (2005) **127**, 9267
83. Janssens, T. V. W., et al., *J. Catal.* (2006) **240**, 108
84. Nowitzki, T., et al., *Surf. Sci.* (2006) **600**, 3595
85. Bligaard, T., et al., *J. Catal.* (2004) **224**, 206
86. Kim, J., et al., *Surf. Sci.* (2006) **600**, 4622
87. Nilsson, A., et al., *Catal. Lett.* (2005) **100**, 111
88. Lin, S. D., et al., *Catal. Lett.* (1993) **17**, 245
89. Yuan, Y., et al., *Catal. Lett.* (1996) **42**, 15
90. Haruta, M., *Catal. Today* (1997) **36**, 153
91. Lee, S.-J., and Gavriilidis, A., *J. Catal.* (2002) **206**, 305
92. Calla, J. T., et al., *J. Catal.* (2006) **238**, 458
93. Overbury, S. H., et al., *J. Catal.* (2006) **241**, 56
94. Yan, Z., et al., *Catal. Lett.* (2006) **111**, 15
95. Ruggiero, C., and Hollins, P., *J. Chem. Soc., Faraday Trans.* (1996) **92**, 4829
96. Gottfried, J. M., et al., *Surf. Sci.* (2003) **536**, 206
97. Kim, J., et al., *J. Phys. Chem. B* (2006) **110**, 17512
98. Biener, J., et al., *ChemPhysChem* (2006) **7**, 1906
99. Xu, C., et al., *J. Am. Chem. Soc.* (2007) **129**, 42
100. Carlsson, A., et al., *J. Phys. Chem. B* (2006) **110**, 5286
101. Matthey, D., et al., *Science* (2007) **315**, 1692
102. Lopez, N., et al., *J. Catal.* (2004) **225**, 86