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Heterogeneous Catalysis

Structural Origin: Water Deactivates Metal Oxides to CO Oxidation and Promotes Low-Temperature CO Oxidation with Metals**

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Water is perhaps the most common molecule in heterogeneous catalysis, as it is unavoidable in almost any system. Interestingly, it can play completely different roles in the presence of either metals or metal oxides,[1–15] which are the two most common types of the catalysts. On one hand, a moderate amount of water on the surface of late-transition metals such as Au, Pt, and Pd, can promote low-temperature CO oxidation, which is one of the hottest topics in catalysis because of the environmental concerns.[1–6] On the other hand, it can be a devastatingly poisonous species on the surface of metal oxides, the best example being the water-induced deactivation on tricobalt tetraoxide (Co_3O_4).[7–15] Specifically, morphology-controlled Co_3O_4[7,16,17] displays extraordinarily high catalytic activity for CO oxidation at very low temperatures (ca. −77 °C). However, in the presence of trace amounts of water its activity is dramatically reduced.[7–12] It is worth emphasizing that transition-metal oxides have received an increasing amount of attention for CO oxidation because of their unexpectedly high catalytic activities, low price, and especially the rich surface chemistry which affords the potential to tune the catalytic properties to a considerable degree.[18–20] Moreover, the poisoning effect of H_2O has also been reported for other oxide-based catalysts such as CuO and MnO_x, and it may well be a common issue in many oxide systems.[13–15] To comprehend the fundamental role of water in heterogeneous catalysis in general, the following questions need to be answered: What is the mechanism of H_2O deactivation on Co_3O_4 oxide? How can one rationalize such a difference between metal and metal oxide systems regarding H_2O effects? Herein we report a thorough investigation uncovering the origin of the deactivation of Co_3O_4 by H_2O and addressing the general effect of H_2O on metal and metal oxides by using first principles calculations.

The deactivation resulting from the presence of water is the main obstacle currently limiting the application of Co_3O_4 to CO oxidation, and the deactivation mechanism is much debated. The following suggestions regarding the water poisoning effect have been proposed:[7–12] 1) water molecules strongly adsorb at the active site, thus blocking the CO adsorption; or 2) water dissociation occurs on the catalyst surface to form a surface OH group that inhibits the adsorption of CO or O_2; or 3) the formation of graphite-type carbon deposits or surface carbonate (CO_3^{2-}) species. However, no consensus has been reached. To the best of our knowledge, there is only one theoretical study reported concerning the deactivation mechanism at the molecular level, and it focused on the competing effect of the molecular adsorption of H_2O at active Co^{3+} sites.[11b] In this work, almost all the possible deactivation pathways of Co_3O_4 with regard to water were investigated and the key roles of the bicarbonate species and surface lattice OH in affecting the catalyst activity were determined. More importantly, together with the results for Co_3O_4 and transition metals, systematic analyses using an energy decomposition model are also given to reveal the origin of the H_2O effect in general.

All the calculations were performed with the Perdew–Wang 91 functional using the VASP code and some energies were checked using the HSE06 functional.[21,22] The calculation details can be found in the Supporting Information. In our previous work,[22] the structure of the active surface, (110), of Co_3O_4 was identified and thus used herein. On (110) surfaces, almost all possible poisoning pathways either suggested or hinted at by a range of experimental work, including the blocking of active sites and the lattice oxygen supply, were studied (Scheme 1).

Molecular adsorption of H_2O at Co^{3+} was first calculated. It was found that the H_2O molecule sits above the Co^{3+} (Path C; Scheme 1) with a chemisorption energy of 0.67 eV, which is much lower than that of CO (1.37 eV), and thus the direct molecular adsorption of H_2O is expected to hardly block Co^{3+} efficiently for CO adsorption. Alternatively, H_2O could dissociatively adsorb onto Co^{3+} through transfer of one H atom to the nearest O_{2c} or O_{3c} and thus leaving the OH on Co^{3+} (Path B; Scheme 1) with an adsorption energy of 1.04 eV and 0.87 eV, respectively, which are still lower than that of CO. However, the reverse reaction barriers of both cases are above 1 eV. With such high barriers, the reverse reactions of these H_2O dissociations may not be facile, and the Co^{3+} may gradually be covered by the OH group. Interestingly, on the Co_3O_4 (110) surface, the Co^{3+} bonding with one OH group can further adsorb another CO molecule to give a geminal adsorption configuration with a chemisorption energy of 1.12 eV (see Figure S1a in the Supporting Informa-

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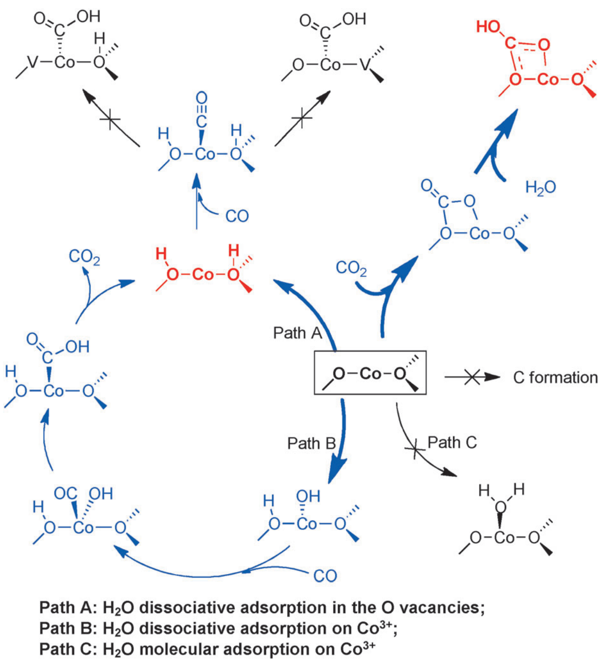

Scheme 1. Illustration of various deactivation pathways for the presence of water on Co_3O_4 as investigated in this work . The structures marked in red are the poisonous species and the pathways ahown in blue indicate the poisonous pathways and the corresponding intermediates. Path A: H_2O dissociative adsorption in the O vacancies; Path B: H_2O dissociative adsorption on Co^{3+} Path C: H_2O molecular adsorption on Co^{3+}.

tion). Whether the Co^{3+} site is efficiently blocked by this OH group depends on the possibility of the following sequence of reactions [Eq. (1) and (2)]:

$$CO^{*}\text{-}Co^{3+}\text{-}OH^{*} \rightarrow Co^{3+}\text{-}COOH^{*} \tag{1}$$

$$Co^{3+}\text{-}COOH^{*} + O_{2c}(O_{3c}) \rightarrow Co^{3+} + CO_2(g) + O_{2c}H(O_{3c}H) \tag{2}$$

Our DFT results show that both steps are facile, thus having a very low barrier of 0.28 eV for COOH formation and approximately 0.1 eV for COOH dehydrogenation to form CO_2 (see Figure S1 in the Supporting Information for the structures of the transition state (TS) and the intermediate species COOH). Therefore, the OH group directly bound to Co^{3+} can be readily removed by CO, and would not lead to a fatal blocking. However, the dissociative adsorption of H_2O at the Co^{3+} site would eventually give rise to the hydrogenation of the surface lattice oxygen. If lattice OH at either the O_{2c} or O_{3c} site was inert toward CO at reaction temperatures, the reaction would not continue.

In our previous work, we showed that O_{3c} can easily react with CO to release CO_2 and form oxygen vacancies.[22] At the site of the vacancies, O_2 can readily adsorb molecularly with a chemisorption energy as high as 2.64 eV or dissociate to fill the oxygen vacancy. In the presence of water, H_2O may compete with the O_2 adsorption to block the vacancy by molecular or dissociative adsorption. It was found that H_2O prefers to dissociate in the O_{3c} vacancy by releasing one H atom to the nearest neighbor, O_{3c}, thus forming two surface OH_{3c} simultaneously. This process gives rise to an energy gain of 1.31 eV and hence the corresponding reverse reaction should be difficult at the reaction temperature. The dissociative adsorption of H_2O at the O_{2c} vacancy to form two adjacent $O_{2c}H$ was also calculated with a high energy gain of 1.84 eV. The net effect of these two pathways is to induce the surface hydration of lattice oxygen, thus surrounding the active Co^{3+} site.

We calculated CO adsorption at the Co^{3+} site in the presence of $O_{2c}H$. The chemisorption energy was found to be 1.55 eV (1.37 eV without OH), thus indicating that the presence of $O_{2c}H$ does not affect CO adsorption but exhibits some level of facilitation. However, the TS of CO + $O_{2c}H$ that was located (Figure 1 a) has a barrier as high as 1.60 eV. Compared with the reaction between CO and the lattice O_{2c} and O_{3c} (the barriers are 0.78 and 0.61 eV, respectively), $O_{2c}H$ is inert at low temperature, thus indicating that the surface O_{2c} sites would be blocked gradually because of the presence of water. It is worth noting that $O_{2c}H$ can easily transfer its H atom to the nearest neighboring O_{2c} by overcoming a barrier as low as 0.35 eV (see TS in Figure 1 c). Therefore, when the coverage of the $O_{2c}H$ species is low, the formation of $O_{2c}H$ does not considerably affect the activity of the catalyst. However, statistically speaking, as $O_{2c}H$ coverage reaches above 0.5 ML, the additional formation of $O_{2c}H$ would give rise to the deactivation at the O_{2c} site.

Similar to the case of $O_{2c}H$, the adsorption of CO in the presence of $O_{3c}H$ was also reasonably strong (1.31 eV), but the direct reaction between the adsorbed CO and $O_{3c}H$

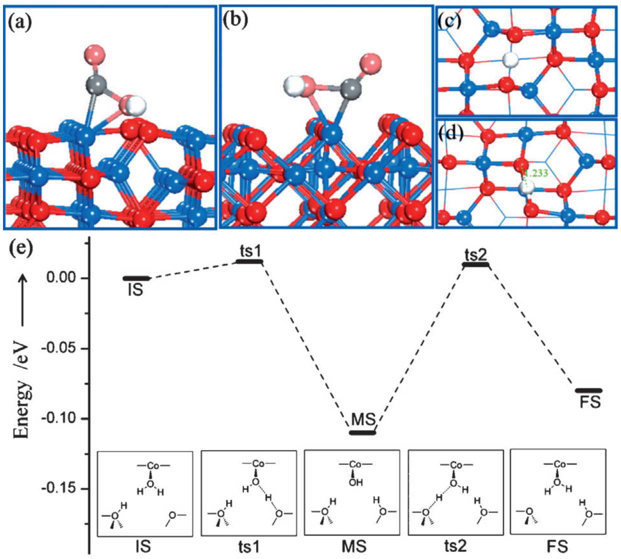

Figure 1. Transition states for CO reacting with OH_{2c} (a) and OH_{3c} (b). Transition states of H transfer to O_{2c} (c) and O_{3c} (d). e) Energy profile for H transfer from O_{3c} to O_{2c} with the help of another H_2O molecule. To clearly show the TS structures of CO reacting with OH, the O in CO and OH are represented in pink. The bottom panel of (e) shows the top view of the corresponding states in the energy profile, in which IS and FS are the initial state ($O_{3c}H$) and final state ($O_{2c}H$) with a nearby water molecule, respectively, and MS is the intermediate state involved in the H transfer from O_{3c} to O_{2c}.

possesses a high barrier (1.32 eV, see TS in Figure 1 b). Thus, $O_{3c}H$ is difficult to remove. However, H in $O_{3c}H$ may diffuse across the surface, thus leaving O_{3c} ready to react with the adsorbed CO on Co^{3+}. To check this possibility, we calculated the diffusion barrier of H from O_{3c} to the nearest O_{3c} or O_{2c}. In contrast to the easy H diffusion between the O_{2c} sites, it is difficult for H in $O_{3c}H$ to diffuse away directly (the diffusion barrier is as high as 0.92 eV, Figure 1 d). We also considered the possibility of an indirect transfer of H in $O_{3c}H$ to the nearest O_{2c} in the presence of a H_2O molecule. An adsorbed H_2O molecule on Co^{3+} site can readily dissociate and pass one H atom to O_{2c} to form a local 'triple-OH' configuration, as shown by the structure in Figure 1 e. H in $O_{3c}H$ can then easily transfer to OH bound to Co^{3+} to reproduce a H_2O molecule. The energy profile of the whole process is plotted in Figure 1 e, which shows that the largest barrier is as low as 0.11 eV and thus this pathway is favorable. Therefore, during the initial reaction stage $O_{3c}H$ may not lead to a fatal poisoning for the CO_2 formation owing to the presence of facile H_2O-assisted H-transfer routes. Unfortunately, as the reaction proceeds, $O_{2c}H$ groups would accumulate, especially when the water content is high (see the Supporting Information). When all the O_{2c} sites on the surface are hydrated, the poisoning effect of surface hydrogenation would be severe. Qualitatively, this is in line with experimental observation[7] showing that the deactivation curve is slow initially, but speeds up rapidly at the latter stage.

Why is OH so inactive compared to lattice O? To answer this question, an energy decomposition analysis was carried out (see the Supporting Information), in which each individual term contributing to the barrier of CO reacting with $O_{3c}H$ was calculated (Table 1). From the data, we can see that the higher barrier of $CO + O_{3c}H$ mainly derives from the activation of $O_{3c}H$ from its initial configuration to the TS, which has an energy cost as high as 1.62 eV. The corresponding term in the case of O_{3c} is only 0.19 eV. This difference can essentially be understood in terms of the geometric effect: For O_{3c}, the formation of the TS requires the O_{3c} activation from the three-coordinated configuration to the two-coordinated one,[22] while for the formation of the TS involving OH_{3c} it is necessary to remove the three-coordinated $O_{3c}H$ in the initial state to sit on the off-top site (see Figure 2 b) of the surface Co^{3+} in the TS, which is difficult to occur.

Table 1: Listed are components of the energy decomposition analyses for CO reacting with O_{3c} and $O_{3c}H$ on a $Co_3O_4(110)$ surface, and CO reacting with surface O and OH on Pt(111) and Pd(111) surfaces, respectively.[a]

	$Co_3O_4(110)$		Pt(111)		Pd(111)	
	O_{3c}	$O_{3c}H$	O	OH	O	OH
ΔE_{CO}	−0.02	0.59	0.57	0.58	0.79	0.88
$\Delta E_{O(OH)}$	0.19	1.62	0.62	0.03	0.63	0.39
ΔE_{int}	0.44	−0.89	−0.14	−0.36	0.30	0.03
E_a	0.61	1.32	1.05	0.25	1.72	1.30

[a] Energies calculated according to $E_a = \Delta E_{CO} + \Delta E_O + \Delta E_{int}$. ΔE_{CO} (ΔE_O) is the activation energy of CO (O) from the initial state to the TS without O (CO) and ΔE_{int} is the interaction energy (see the Supporting Information). Values reported in eV.

It is worth discussing the role of surface carbonate (CO_3^{2-}) and carbons deposit in the deactivation.[7–10] We found that carbonate formation from CO_2 adsorption should not induce a fatal deactivation because of the low adsorption energy. Interestingly, our results show that the carbonate may readily convert into a bicarbonate species (HCO_3^-) in the presence of water, by overcoming a small barrier and being strongly exothermic (see details in the Supporting Information). Because of its high stability, bicarbonate can be expected to be an important blocking species on Co^{3+} sites. Regarding the carbon formation, we calculated the possibility of it blocking the exposed Co^{3+} site or surface O vacancy, and the results show that it may not be an important deactivation route owing to high reaction barriers (see the Supporting Information).

Having obtained the detailed H_2O-indued deactivation mechanisms on Co_3O_4, we are in a position to extend our investigation to metal catalysts, with the aim of obtaining a comprehensive understanding of the effect of H_2O in heterogeneous catalysis in general. One of the key deactivation factors of Co_3O_4 can be ascribed to the hydrogenation of the surface lattice O, that is, formation of surface OH group on the oxide surface, which is inert toward CO oxidation at low temperature relative to the surface lattice O. As mentioned above, H_2O on CuO or MnO_x was found to lead to an adverse effect on CO oxidation, and water poisoning may be a general problem in oxide systems. However, experimental results showed that on the platinum group metal surfaces such as Pt and Pd the presence of H_2O considerably facilitates CO oxidation at lower temperatures.[5,6] How can we understand this difference? On transition-metal surfaces, the key factor in affecting the overall activity of CO oxidation at low temperature is the relatively high barrier of adsorbed CO reacting with surface atomic O ($CO^* + O^* \rightarrow CO_2$). The presence of H_2O provides an alternative reaction channel, as shown in Equations (3)–(6).

$$H_2O + {}^* \rightarrow H_2O^* \tag{3}$$

$$O^* + H_2O^* \rightarrow 2\,OH^* \tag{4}$$

$$CO^* + OH^* \rightarrow COOH^* + {}^* \tag{5}$$

$$COOH^* + OH^* \rightarrow CO_2 + H_2O^* + {}^* \tag{6}$$

To compare the water effects on metal and metal oxide surfaces, we calculated these elemental reactions on four common metal surfaces, namely Pd(111), Pt(111), Ir(111), and Rh(111). The results are summarized in Table 2, and we can see that surface O can readily react with H_2O to form OH, which can further react with CO through a smaller barrier, compared to that of the reaction $CO + O \rightarrow CO_2$, to yield reactive COOH. Taking Pt(111) as an example, the barrier for CO to react with O is 1.05 eV. However, it is significantly reduced to 0.25 eV for CO reacting with OH. The energy profile illustrated in Figure 2 c shows that the reaction channel involving an OH species, resulting from the presence of H_2O,

Table 2: Calculated reaction barriers of the key reaction steps involved in CO oxidation with and without H_2O.[a]

	Pt(111)	Pd(111)	Ir(111)	Rh(111)
$CO^* + O^* \rightarrow CO_2$	1.05	1.72	0.85	1.36
$E_{ad}(H_2O)$	0.23	0.27	0.28	0.36
$O^* + H_2O^* \rightarrow 2\,OH^*$	0.31	0.47	0.23	0.29
$CO^* + OH^* \rightarrow COOH^*$	0.25	1.29	0.17	0.98
$COOH^* + OH^* \rightarrow CO_2 + H_2O^*$		ca. 0.10		

[a] Values reported in eV.

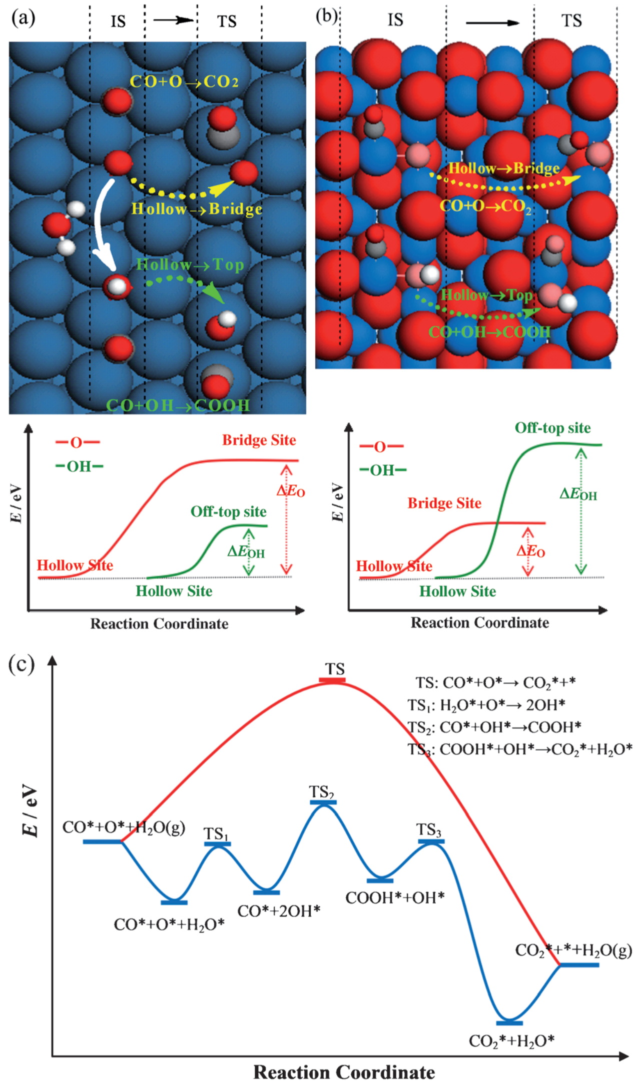

Figure 2. a) The top panel illustrates the movement of surface O and OH species in forming their respective transition states from the initial states (hollow sites) by reacting with CO on metal surface; the lower panel gives the corresponding energy variation during the activation process of O and OH. b) Similar to (a), the top and lower panel show the structure and energy information of lattice O and OH movement in reacting with CO to form the transition states from the intial states on Co_3O_4(110) surface, respectively. c) Energy profiles illustrating CO oxidation with (blue) and without (red) H_2O on metal surfaces, involving the key reaction steps of CO reacting with O ($CO^* + O^* \rightarrow CO_2^*$) or OH ($CO^* + OH^* \rightarrow COOH^*$), respectively.

has no high barriers in the whole process. It is clear that H_2O plays an essential catalytic role in metal systems.

An obvious question is why the effect of the OH species on CO oxidation activity is so different for metal versus metal oxide surfaces. To solve this puzzle, we analyzed the origin of the reduced barrier of CO reacting with OH on Pt and Pd surfaces as examples for comparison with that for CO reacting with surface O on Co_3O_4. The results are listed in Table 1. As shown in the table, the barrier reduction on the metal surfaces mainly comes from the activation of oxidizing species O and OH in forming the TS from the initial states; 0.62 eV versus 0.03 eV on Pt(111) and 0.63 eV versus 0.39 eV on Pd(111).

As in the case of Co_3O_4, O must be moved from the threefold hollow site to the bridge site in forming the TS, while OH must be activated from the hollow site to the off-top site (Figure 2). The potential energy surfaces of OH adsorbed at various sites on metal surfaces are rather flat compared with those of the O species. However, on oxide surfaces such as Co_3O_4 (Table 1), the potential energy surface of OH located at different sites varies sharply: In forming the TS for CO + OH, OH needs to be removed from the hollow site (creating an O vacancy cavity) to the off-top site of a surface metal cation. This energetically demanding geometric requirement, in conjunction with the rough potential energy surface of OH on the oxide, is the key factor that gives rise to the higher barrier on oxides, as illustrated in Figures 2 a and b.

In summary, this work represents the first systematic theoretical study of the H_2O effect on low-temperature CO oxidation. It has been found that for Co_3O_4 the reactivity of surface OH, formed as a result of the presence of H_2O in the system, is much lower than that of lattice O, thus giving rise to the deactivation, whereas the formation of stable bicarbonates can block the active Co^{3+}, thus leading to additional deactivation. A scheme showing the enrgy decomposition of the barriers is introduced to quantitatively understand the activity difference between the surface OH and lattice O, thus demonstrating that the origin of activity variance lies in the geometric structures. A fundamental issue in heterogeneous catalysis, namely that H_2O is generally a promoter on metal surfaces for CO oxidation at low temperature but a poisoning species on metal oxides, has also been addressed in this work: The significant difference in the potential energy surfaces of OH on metal and metal oxides is identified to be the origin. Given that water is such a common molecule, the structural effects of O and OH as revealed in our unique energy decomposition analyses are of significance in catalysis, and the understanding obtained from this work may be of general importance.

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[1] a) Q. Sun, *Phys. Rev. B* **2003**, *67*, 205424; b) C. Stampfl, M. V. Ganduglia-Pirovano, K. Reuter, M. Scheffler, *Surf. Sci.* **2002**, *500*, 368.

[2] a) M. Mavrikakis, P. Stoltze, J. K. Norskov, *Catal. Lett.* **2000**, *64*, 101; b) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896; c) M. Neurock, *J. Catal.* **2003**, *216*, 73.

[3] a) M. Daté, M. Okumura, S. Tsubota, M. Haruta, *Angew. Chem.* **2004**, *116*, 2181; *Angew. Chem. Int. Ed.* **2004**, *43*, 2129; b) M. A. Sanchez-Castillo, C. Couto, W. B. Kim, J. A. Dumesic, *Angew. Chem.* **2004**, *116*, 1160; *Angew. Chem. Int. Ed.* **2004**, *43*, 1140; c) H. H. Kung, M. C. Kung, C. K. Costello, *J. Catal.* **2003**, *216*, 425.

[4] a) A. Bongiorno, U. Landman, *Phys. Rev. Lett.* **2005**, *95*, 106102; b) R. A. Ojifinni, N. S. Froemming, J.-L. Gong, M. Pan, T. S. Kim, J. M. White, G. Henkelman, C. B. Mullins, *J. Am. Chem. Soc.* **2008**, *130*, 6801.

[5] a) J. Bergeld, B. Kasemo, D. V. Chakarov, *Surf. Sci.* **2001**, *495*, L815; b) A. Manasilp, E. Gulari, *Appl. Catal. B* **2002**, *37*, 17; c) X.-Q. Gong, P. Hu, R. Raval, *J. Chem. Phys.* **2003**, *119*, 6324; d) S. D. Ebbesen, B. L. Mojet, L. Lefferts, *J. Catal.* **2007**, *246*, 66.

[6] a) F.-X. Liang, H.-Q. Zhu, Z.-F. Qin, H. Wang, G.-F. Wang, J.-G. Wang, *Catal. Lett.* **2008**, *126*, 353; b) S. D. Ebbesen, B. L. Mojet, L. Lefferts, *Phys. Chem. Chem. Phys.* **2009**, *11*, 641.

[7] X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, *Nature* **2009**, *458*, 746.

[8] Y. B. Yu, T. Takei, H. Ohashi, H. He, X. L. Zhang, M. Haruta, *J. Catal.* **2009**, *267*, 121.

[9] a) J. Jansson, *J. Catal.* **2000**, *194*, 55; b) J. Jansson, M. Skoglundh, E. Fridell, P. Thormählen, *Top. Catal.* **2001**, *16/17*, 385.

[10] D. A. H. Cunningham, T. Kobayashi, N. Kamijo, M. Haruta, *Catal. Lett.* **1994**, *25*, 257.

[11] a) S. C. Petitto, E. M. Marsh, G. A. Carson, M. A. Langell, *J. Mol. Catal. A* **2008**, *281*, 49; b) X. L. Xu, J. Q. Li, *Surf. Sci.* **2011**, *605*, 1962.

[12] F. Grillo, M. M. Natile, A. Glisenti, *Appl. Catal. B* **2004**, *48*, 267.

[13] G. Y. Wang, W. X. Zhang, Y. C. Cui, H. L. Lian, D. Z. Jiang, T. H. Wu, *Chin. J. Catal.* **2001**, *22*, 408.

[14] a) D. Gamarra, A. Martinez-Arias, *J. Catal.* **2009**, *263*, 189; b) H. Zou, X. Dong, W. Lin, *Appl. Surf. Sci.* **2006**, *253*, 2893.

[15] K. Sirichaiprasert, A. Luengnaruemitchai, S. Pongstabodee, *Int. J. Hydrogen Energy* **2007**, *32*, 915.

[16] a) Y. Ren, Z. Ma, L. P. Qian, S. Dai, H. Y. He, P. G. Bruce, *Catal. Lett.* **2009**, *131*, 146; b) H. Tüysüz, M. Comotti, F. Schüth, *Chem. Commun.* **2008**, 4022.

[17] C. Y. Ma, Z. Mu, J. J. Li, Y. G. Jin, J. Cheng, G. Q. Lu, Z. P. Hao, S. Z. Qiao, *J. Am. Chem. Soc.* **2010**, *132*, 2608.

[18] S. Royer, D. Duprez, *ChemCatChem* **2011**, *3*, 24–65.

[19] a) J. Kašpar, P. Fornasiero, M. Graziani, *Catal. Today* **1999**, *50*, 285; b) H.-F. Wang, Y.-L. Guo, G.-Z. Lu, P. Hu, *Angew. Chem.* **2009**, *121*, 8439; *Angew. Chem. Int. Ed.* **2009**, *48*, 8289.

[20] J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, M. Pérez, *Science* **2007**, *318*, 1757.

[21] a) G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251; b) G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15; c) J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2006**, *124*, 219906.

[22] H.-F. Wang, R. Kavanagh, Y.-L. Guo, Y. Guo, G. Z. Lu, P. Hu, *J. Catal.*, revised.