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Bridging Nanoscience and Surface Science to Understand Heterogeneous Catalysis

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Introduction

Supported nanometer scale clusters¹ consist one of the most promising classes of materials, with wide applications not only in chemistry^{2,3} but also in physics⁴ and biology.⁵ Such nanostructured materials used in heterogeneous catalysis, a research field link to polymerization of olefins⁶ represent a transition between the individual molecules and bulk solids, and have unique catalytic⁷ or physical⁸ properties. More precisely, heterogeneous supported metal catalysts⁹ consist of a porous oxide such as alumina with a large specific area (>200 m²/g) on which metal nanoparticles are dispersed. Among the several major industrial uses, note that this family of materials is used in environmental applications.¹⁰ Atomic scale data being required to understand of the catalytic mechanisms, synchrotron radiation related techniques and more precisely X-ray absorption spectroscopy (XAS) has been widely used.¹¹ XAS, encompassing both the study of the near edge region and the fine structure region at energies above the absorption edge, has proven invaluable in understanding the structure of catalysts while the reaction occurs.^{12,13}

In this paper, the ultimate goal is to build a bridge between surface science and nanosciences to understand heterogeneous catalysis. In a previous paper,¹⁴ we proposed that a link exists between two parameters :

- the nature of the adsorption mode of the NO molecule on metallic surfaces which can be either dissociative or non dissociative. Its knowledge comes from surface science,¹⁵
- the behaviour of the nanometer scale metallic cluster following the NO adsorption. We distinguish at least three dif-

ferent cases. The metallic cluster can be stable versus this adsorption, a sintering process of the metallic cluster can occur or a disruption of the metal-metal bonds in response to this adsorption can be observed.

This intimate link which exists between the adsorption mode and the behaviour of the cluster is finally used to discuss the evolution versus time of the catalytic activity.

Synchrotron Radiation Related Techniques

Catalyst characterization is the cornerstone of the science of catalysis. Thus, several excellent publications have been dedicated to the characterization techniques used in heterogeneous catalysis.¹⁶ The usual characterization techniques help to delimit the problem but do not precisely show the evolution of the structural and electronic characteristics of the metallic particles while the chemical reaction occurs. In fact, modern approaches include almost systematically synchrotron radiation related techniques.¹⁷ It is quite difficult to quote all of them but we can at least distinguish Fourier transform-infra red spectroscopy,¹⁸ soft XAS,¹⁹ *in-situ* time-resolved dispersive XAS (DXAS),²⁰ anomalous wide angle X-ray scattering²¹ and anomalous small angle X-ray scattering.²²

Among all these different synchrotron techniques,²³ XAS²⁴ has several specific advantages. Regarding the edge part of the absorption spectrum, several physical parameters affect the position as well as the morphology of the edge : the size and the shape of the cluster, which can be considered as an intrinsic effect (density of states in Pt nanoparticles is significantly different from that of bulk Pt), and a possible charge transfer between the cluster and the support, which is considered as an extrinsic effect.²⁵ Thus, special attention has to be paid if a simulation of the edge is performed with a linear combination of the edge of well-crystallised reference compounds.²⁶ For metal nanoparticles,²⁷ the knowledge of the different structural parameters (i.e. average co-ordination numbers and interatomic distances), allows us to determine the cluster size, morphology and the degree of relaxation.

Some Generalities on the Adsorption Process

When a diatomic molecule such as NO approaches a metal surface,¹⁵ it may encounter three kinds of potential wells corresponding respectively to a physisorbed state (far from the surface), a molecular chemisorbed state and finally to a dissociative chemisorption state. Dissociative chemisorption is the most stable situation if

$$|E_{ads}(N)| + |E_{ads}(O)| > E_{dis}(NO) + |E_{ads}(NO)|$$

where $E_{ads}(X)$ is the atomic adsorption energy (<0) of atom

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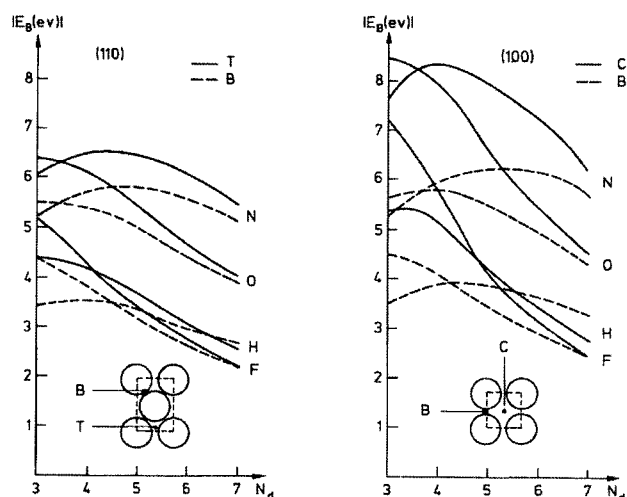


Figure 1. Binding energies of N, O, F, and H for different sites on (110) and (100) BCC transition metal surfaces as a function of the number N_d of d electrons (from ref. 15).

X while $E_{dis}(\text{NO})$ and $E_{ads}(\text{NO})$ are respectively the dissociation energy (>0) of the free molecule and the molecular chemisorption energy (<0). The term $E_{dis}(\text{NO})$ is obviously independent of the nature of the metal. The adsorption energies (Figure 1) are more important for metals which are at the middle of the transition series, metals for which we observed here a dissociative adsorption.

This is a general tendency and the evolution of atomic adsorption energy versus the number of electrons in the d band is almost the same for the elements N, O, and also C. We can note that the frontier between nondissociative and dissociative adsorption can be given roughly by the dissociation energy of the molecule of interest. For example, regarding the 3d transition elements, the frontier is between Fe and Co for N_2 and between Ni and Cu for NO, a tendency in line with the different values of the dissociation energy of these two molecules ($\text{N}_2=9.76$ eV, $\text{NO}=6.50$ eV). Regarding the adsorption of O_2 on nanometer scale metallic clusters, the different experiments done with XAS shows that even Pt clusters are not stable versus the adsorption of O_2 . At this dimension, it seems that there is no “noble” metals, an observation in line with the low value of the dissociation energy of this molecule ($\text{O}_2=5.12$ eV).

Now, we would like to consider the relationship between the adsorption mode of the molecule and the behaviour of the cluster for simple molecules, namely NO and CO.

NO Adsorption on Metallic Nanoclusters

Combining recent calculations of the electronic structure of nanometer-scale metallic clusters with the suggestion of Brown²⁸ relating the melting point to the ability of metallic surfaces to dissociate NO, we have proposed a relationship

between the adsorption mode (dissociative or molecular) of NO at room temperature and the behaviour of nanometer-scale metallic particles (sintering or disruption) in response to this adsorption.

Considering a range of elements, a straight line separates two possibilities : associative adsorption of NO accompanied by sintering of the particles and dissociative adsorption accompanied by particle fragmentation. If this initial model was only supported by experimental data on Pt^{29,30} and Ru,³¹ a second set of publications is in line with this relationship. More precisely, experiments performed on the following nanomaterials: Rh/SiO₂,³² Rh/ γ -Al₂O₃,³³ Ir/H-ZSM-5³⁴ as well as Cu/Al₂O₃,³⁵ Pt/SiO₂³⁶ are coherent with this simple model. An interesting case is given by palladium. On a perfect Pd(111) surface, NO adsorbs molecularly³⁷ while molecular adsorption and dissociation strongly compete on Pd(100)³⁸ and Pd(110)³⁹ surfaces. The position of Pd versus the straight line (on Figure 2) is thus not defined. Consequently, it is not really a surprise if the behaviour of Pd clusters can vary. For example, for Pd particles supported on Al₂O₃/NiAl(110), no overall morphological changes of the nanocrystals were observed during NO gas exposure⁴⁰ while for Pd particles deposited on CeO_x/Al₂O₃, the formation of PdO bonds are observed.⁴¹

Now we would like to discuss the limits as well as the advantages of this simple model. Special attention has to be paid to the adsorption temperature as well as to the cluster

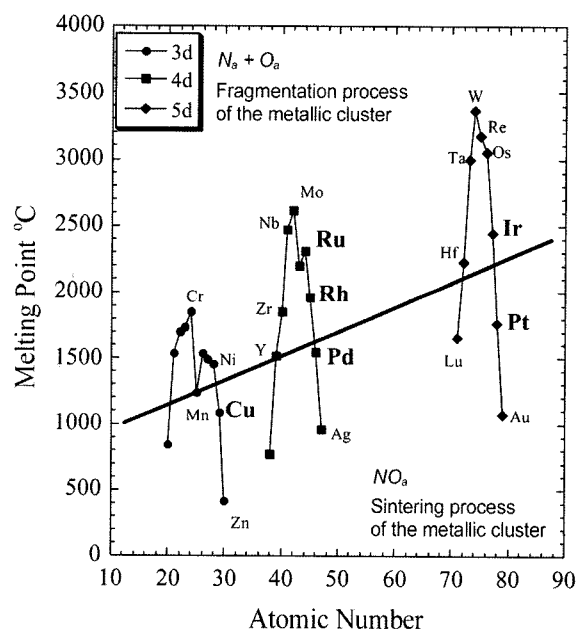


Figure 2. Diagram showing a correlation between the adsorption mode and the behaviour of a cluster based on experimental data regarding the elements Cu, Ru, Rh, Ir, and Pt. A straight line separates the two adsorption modes : dissociative and non dissociative (from ref. 14).

size. However, this relationship seems to be independent of the preparation procedure as well as the nature of the support.

The adsorption temperature is one key parameter. This parameter affects the adsorption mode as well as the stability of the metal oxide particle. For example, NO adsorbs molecularly on Rh at low temperatures and dissociatively at higher temperatures. On Rh[100], molecular NO dominates upon adsorption at 100 K, but heating leads to N₂ and O₂ production, suggesting dissociation. On nickel, molecular adsorption takes place at low temperature whilst at higher temperatures both molecular and dissociative adsorption are observed. Note that the temperature may affect the stability of metal oxide particle through the decomposition process. Also, it is well known that the catalytic activity is size dependent.¹⁰ We have here to point out that most of the experiments have been performed through XAS on very small clusters with a dispersion close to 100%.

To a first approximation, this relationship seems independent of the preparation procedure and more precisely of the precursor as well as the nature of the support. The different precursors used in these previous works are the following Ru₃(CO)₁₂, IrCl₃(H₂O)₃, Ir(NH₃)_xCl₃(H₂O), RhCl(CO)₂, H₂PtCl₆, Pt(NH₃)₄(OH)₂. In the case of copper, we have even a physical procedure (evaporation). In addition, nanometer scale metallic clusters are supported on a wide range of support: γ -Al₂O₃ (Ru), H-ZSM-5 (Ir), γ -Al₂O₃, ZrO₂, CeO₂ (Rh), Al₂O₃ (Cu), Al₂O₃, SiO₂ (Pt).

We have proposed two different mechanisms. For metals below the straight line (Figure 2), we may observe a structural situation close to the one observed by K. Asakura *et al.*⁴² in the case of platinum i.e. atomic species linked to several NO molecules. Then, the mobility of the nitrosyl species over the surface of the support leads to the formation of large clusters. At the opposite, when we consider metals above the line, according to the work of T. Campbell *et al.*³³ the metallic atoms may have bonds either to oxygen or nitrogen atoms. At high temperature, the formation of a metallic oxide can be observed due to desorption of nitrogen species.

Adsorption of CO Molecules

First, as for the NO molecule, we would like to consider the adsorption process on a metallic surface. On Table I, the ability of transition metal surface to dissociate the CO molecule has been reported from the work by R.B. Anderson.⁴³ As for the NO molecule, metals at the end of the series are

Table I. Ability of Transition Metal Surfaces to Dissociate the CO Molecule at Room Temperature from R.B. Anderson⁴³

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au

associated to a non dissociative adsorption process (metals in bold characters). If we consider this ability of transition metals to dissociate the CO molecule at higher temperature, namely 200-300 °C, only the metals which are underlined are associated with a non dissociative adsorption mode. At this point, we have to consider the behaviour of metal clusters versus the CO adsorption.

On Pt clusters, A. Berko *et al.*⁴⁴ found that CO adsorption induces a significant increase in the initial size of the Pt nanoparticles of 1-2 nm even at room temperature. This agglomeration preceded by disruption of the smaller Pt nanoclusters at lower CO pressures is explained by CO-assisted Ostwald ripening, in which the mass transport proceeds via surface carbonyl intermediates. Similar results have been obtained in the case of ruthenium by T. Mizushima *et al.*⁴⁵ Adsorption of CO at room temperature results in a drastic change of local structure around Ru atoms : Ru-Ru bonds are disrupted and Al-O-Ru-(CO)_n (n=1-2) is formed. When the temperature is raised, Ru atoms agglomerate and small metal clusters are recovered. In the case of rhodium, the CO-induced disintegration process of Rh clusters on an Al₂O₃ surface has been observed in the case of static experiments⁴⁶ as well as by DXAFS.⁴⁷ Finally, note that the formation of Cu metallic clusters induced by CO adsorption has been also pointed out.⁴⁸ As for Pd clusters, several studies^{49,50} have noticed -CO adsorption driven growth in supported Pd clusters.

For all these metals, we are in the case of a non dissociative adsorption mode and it seems that the structural evolution of the nanometer scale metallic atoms follows the same scheme. Based on all these experimental facts, we can suppose that CO adsorption leads to a disruption of metal-metal atoms and to the formation of Metal-(CO)_n species. Then, metallic clusters can be observed and as supposed in the case of Pt, mass transport proceeds via surface carbonyl intermediates. This general schema is quite close to the one proposed in the case of NO adsorption process.

What happens if we consider metals which displays a dissociative adsorption mode. A beginning of the answer is given by the study performed by O. Ducreux *et al.*⁵¹ on the Co/Al₂O₃ system. Through *in situ* X-ray diffraction experiments, the formation of a carbide is pointed out.

On the Way to Discuss the Catalytic Activity

Is it possible to extract, from the NO adsorption process alone, some information regarding the catalytic activity of the metallic clusters from this purely energetic approach? For metals above the stability line, NO adsorption leads to the formation of a metal oxide. Thus, the catalytic activity tends to decrease. This conclusion is in line with the experimental results obtained by T. Campbell *et al.*³³ On the contrary, for metals below the line, large metallic clusters are

finally generated and evolution of the catalytic activity will follow these structural modifications.

What kind of information do we have regarding the metal-support interaction? As we have seen the relationship we have proposed between the adsorption mode of NO and the behaviour of the metallic cluster seems to be independent of the nature of the support, except for palladium. For this metal, a great difference exists between MgO and CeO₂. We have linked this dependency to the position of the metal versus the line which separates the two adsorption modes. If this assumption is correct, this dependency is not so significant for other metals for which the position versus the straight line (Figure 2) is more clear, namely Rh or Pt.

Is it possible to select some bimetallic catalysts? This purely energetic model leads to a complete rejection of some bimetallic systems. For example, if we consider a RhRu bimetallic cluster (or a RhIr as well as RuIr bimetallic), the NO adsorption process leads probably to the formation of a metal oxide i.e. the dissociation of NO will stop. On the other hand, if we consider a PtCu system, it is probable that the NO adsorption will lead to large clusters. A guideline for the choice of the bimetallic system is to add to platinum a second metal such Rh or Ru. If we consider the CeO₂ support, the PtPd bimetallic seems to be acceptable while the PtPd system supported on alumina has to be rejected.

Is it possible to use this simple model to predict the behaviour of the metal nanoparticles when a mixture of NO+O₂ is considered? For Rh, on which NO molecules undergo dissociative adsorption with the formation of metal-oxygen bond formation, it is possible that the presence of oxygen will not change significantly this simple scheme. Such behaviour is expected for other metals such Ru or Rh. In contrast, for Pt the situation is more complex because the temperature plays a significant role. In a recent paper, we have studied the effect of gas mixtures (NO+O₂) with excess oxygen. XAS gives a direct structural evidence of a Pt/O substitution in the Pt environment. However, some Pt-Pt bonds persist till 300 °C, which was not the case when oxygen was present alone. Thus, the presence of NO allowed the Pt particles to conserve a metallic character. Note that the relative concentrations of the two gases, as well as the temperature, are probably significant parameters. To a first approximation, we can conclude that for metals above the straight line (Figure 2), namely Rh, Ru or Ir, it is necessary to add to a NO+O₂ mixing, a reducing agent in order to reestablish the metallic state of the atoms. This is not the case for metals below the line (Pt,Cu). In this case, we can probably adjust the relative concentration of the two gases NO and O₂ to keep a metallic state of the Pt (or Cu) atoms.

We can also consider the reaction NO+C₃H₆. For Rh/TiO₂ catalysts, as noticed by Th. I. Halkides,⁵² reduction of NO requires the presence of reduced Rh sites and the role of the hydrocarbon is to remove adsorbed oxygen and restore the

catalytically active sites. This point is clearly in line with a dissociation mode of NO on Rh clusters. We have also performed similar experiments on Pt clusters.⁵³ Although carbon and/or oxygen neighbours appear around Pt, platinum atoms still exist around the central Pt atoms. It seems thus that the catalytic activity associated to these two catalysts may be understood through the link we have suggested between the NO adsorption mode and the behaviour of the metallic cluster.

Conclusions

Here, we have considered the adsorption of simple molecules such NO and CO on nanometer scale metallic cluster and discussed the possibility of an intimate relationship between the adsorption mode and the behaviour of the cluster. Even if parameters such the pressure⁵⁴ which play a significant role have not been discussed, it seems that several experimental results regarding different transition elements are in line with this purely energetic model. At this point, it is worth repeating that all the above assumptions have to be confirmed by experimental results. Finally, it is quite clear that the opportunities given by synchrotron radiation related techniques are well suited to pursue this line of reasoning.

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References

- (1) *Nanotechnology in Catalysis*, G. A. Somorjai, S. Hermans, and B. Zhou, Eds., Kluwer, New York, 2003.
- (2) L. Guzzi, *Catal. Today*, **101**, 53 (2005).
- (3) J. D. Grunwaldt and B. S. Clausen, *Topics Catal.*, **18**, 37 (2002).
- (4) C. R. Henry, *Surf. Sci. Rep.*, **31**, 231 (1998).
- (5) B. K. Maiti, K. Pal, and S. Sarkar, *Inorg. Chem. Com.*, **7**, 1027 (2004).
- (6) R. A. Hutchinson, C. M. Chen, and W. H. Ray, *J. Appl. Polym. Sci.*, **44**, 1389 (2003).
- (7) C. Burda, X. Chen, R. Narayanan, and M. A. El-Sayed, *Chem. Rev.*, **105**, 1025 (2005).
- (8) X. Zhao, D. Ceresoli, and D. Vanderbilt, *Phys. Rev. B*, **71**, 85107 (2005).
- (9) B. C. Gates, *J. Mol. Cat. A*, **163**, 55 (2000).
- (10) F. Garin, *Appl. Catal. A*, **222**, 183 (2001).

- (11) A. E. Russell and A. Rose, *Chem. Rev.*, **104**, 4613 (2004).
- (12) J. Lynch, *Oil & Gas Science and Technology*, **57**, 281 (2002).
- (13) J. D. Grunwaldt, M. Caravati, S. Hannemann, and A. Baiker *Phys. Chem. Chem. Phys.*, **6** (2004).
- (14) D. Bazin, in ref. 1
- (15) M. C. Desjonqueres and D. Spanjaard, *Concept in Surface Physics*, Ed. Springer-Verlag, 1998.
- (16) T. Shido and R. Prins, *Cur. Op. in Sol. Sta. and Mat. Science*, **3**, 330 (1998).
- (17) C. C. Shih and J. R. Chang, *Mat. Chem. and Phys.*, **92**, 89 (2005).
- (18) E. Chouparova, A. Lanzirrotti, H. Feng, K. W. Jones, N. Marinkovic, C. Whitson, and P. Philp, *Energy & Fuels*, **18**, 1199 (2004).
- (19) D. Bazin and L. Guzzi, *Appl. Catal. A*, **213**, 147 (2001).
- (20) A. Suzuki, A. Yamaguchi, T. Chihara, Y. Inada, M. Yuasa, M. Abe, M. Nomura, and Y. Iwasawa, *J. Phys. Chem. B.*, **108**, 5609 (2004).
- (21) D. Bazin, L. Guzzi, and J. Lynch, *Appl. Catal. A*, **226**, 87 (2002).
- (22) A. Braun, J. Ilavsky, B. C. Dunn, P. R. Jemian, F. E. Huggins, E. M. Eyring, and G. P. Huffman, *J. Appl. Cryst.*, **38**, 132 (2005).
- (23) D. Bazin, D. Sayers, and J. Rehr, *J. Phys. Chem.*, **101**, 11040 (1997).
- (24) D. A. Sayers, F. W. Lytle, and E. A. Stern, *Advances in X-ray Analysis*, Ed. Plenum, New-York, Vol 13, 1970.
- (25) D. Bazin, D. Sayers, J. Rehr, and C. Mottet, *J. Phys. Chem.*, **100**, 5332 (1997).
- (26) D. Bazin and J. Rehr, *J. Phys. Chem. B*, **107**, 12398 (2003).
- (27) D. Bazin, J. Lynch, and M. Ramos-Fernandez, *Oil & Gas Science and Technology Rev. IFP*, **58**, 683 (2003).
- (28) W. Brown and D. A. King, *J. Phys. Chem. B.*, **104**, 2578 (2000).
- (29) S. Schneider, D. Bazin, F. Garin, G. Maire, H. Dexpert, G. Meunier, R. Noirot, and M. Capelle, *Appl. Catal.*, **189**, 139 (1999).
- (30) P. Loof, B. Stenbom, H. Norden, and B. Kasemo, *J. Catal.*, **44**, 60 (1993).
- (31) T. Hashimoto, H. Hayashi, Y. Udagawa, and A. Ueno, *Physica B*, **208/209**, 683 (1995).
- (32) K. R. Krause and L. D. Schmidt, *J. Catal.*, **140**, 424 (1993).
- (33) T. Campbell, A. J. Dent, S. Diaz-Moreno, J. Evans, J. Fiddy, M. A. Newton, and S. Turin, *Chem. Comm.*, 30 (2002).
- (34) C. Wogerbauer, M. Maciejewski, and A. Baiker, *J. Catal.*, **205**, 157 (2002).
- (35) S. Haq, A. Carew, and R. Raval, *J. Catal.*, **221**, 204 (2004).
- (36) X. Wang, S. M. Sigmon, J. J. Spivey, and H. H. Lamb, *Catal. Today*, **96**, 11 (2004).
- (37) R. D. Ramsier, Q. Gao, H. N. Waltenburg, K. W. Lee, O. W. Nooij, L. Lefferts, and J. T. Yates, *Surf. Sci.*, **320**, 209 (1994).
- (38) S. Sugai, H. Watanabe, T. Kioka, H. Miki, and K. Kawasaki, *Surf. Sci.*, **259**, 109 (1991).
- (39) R. G. Sharpe and R. Bowker, *Surf. Sci.*, **360**, 21 (1996).
- (40) K. Højrup Hansen, Z. Sljivananin, E. Laesgsgaard, F. Besenbacher, and I. Stensgaardet, *Surf. Sci.*, **505**, 25 (2002).
- (41) J. H. Holles and R. J. Davis, *J. Phys. Chem. B.*, **104**, 9653 (2000).
- (42) K. Asakura, W. J. Chun, M. Shirai, K. Tomishige, and Y. Iwasawa, *J. Phys. Chem. B*, **101**, 5549 (1997).
- (43) R. B. Anderson *The Fischer-Tropsch Synthesis*, Chap 4, Academic Press, New York, 1984
- (44) A. Berko, J. Szoko, and F. Solymosi, *Surface Science*, **566-568**, 337 (2004).
- (45) T. Mizushima, K. Tohji, Y. Udagawa, and A. Ueno, *J. Phys. Chem.*, **94**, 4980 (1990).
- (46) H. F. J. Van't Blik, J. B. A. D. Van Zon, T. Hulzinga, J. C. Vis, D. C. Koningsberger, and R. Prins, *J. Phys. Chem.*, **87**, 2264 (1983).
- (47) A. Suzuki, Y. Inada, A. Yamaguchi, T. Chihara, M. Yuasa, M. Nomura, and Y. Iwasawa, *Angew. Chem. Int. Ed.*, **42**, 4795 (2003).
- (48) X. Wang, J. C. Hanson, A. I. Frenkel, J.-Y. Kim, and J. A. Rodriguez, *J. Phys. Chem. B*, **108**, 13667 (2004).
- (49) S. L. Anderson, T. Mizushima, and Y. Udagawa, *J. Phys. Chem.*, **95**, 6603 (1991).
- (50) W. Vogel, H. Knozinger, B. T. Carvill, W. M. H. Sachtler, and Z. C. Zhang, *J. Phys. Chem. B*, **102**, 1750 (1998).
- (51) O. Ducreux, PhD Thesis, University Paris VI, 1999.
- (52) Th. I. Halkides, D. I. Kondarides, and X. E. Verykios, *Catal. Today*, **73**, 213 (2002).
- (53) S. Schneider, D. Bazin, G. Meunier, R. Noirot, M. Capelle, F. Garin, and G. Maire, *Catal. Lett.*, **71**, 3 (2001).
- (54) Y. Chen, D. Ciuparu, S. Lim, Y. Yang, G. L. Haller, and L. Pfefferle, *J. Catal.*, **226**, 351 (2004).