EINDHOVEN UNIVERSITY OF TECHNOLOGY

Computational study of zeolite-proton-palladium chemistry

Citation for published version (APA):
Harmsen, R. J., Bates, S. P., & Santen, van, R. A. (1997). Computational study of zeolite-proton-palladium chemistry. *Faraday Discussions*, *106*, 443-450. https://doi.org/10.1039/a701789h

DOI:
10.1039/a701789h

Document status and date:
Published: 01/01/1997

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 04. Oct. 2023

Faraday Discuss., 1997, **106**, 443–450

Computational study of zeolitic-proton–palladium chemistry

Roelant Harmsen, Simon Bates and Rutger A. van Santen
Schuit Institute of Catalysis, Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P. O. Box 513, 5600 MB, The Netherlands

A density functional theory study of the interaction of a Pd atom with the zeolitic Brønsted acid site is reported. Whereas reduction of Pd^{2+} to Pd^0 and $2H^+$ is strongly exothermic, the energy of exchange of a single proton between Pd^0 and the zeolite is found to be nearly thermodynamically neutral. Reaction energy diagrams are presented for proton-assisted CO hydrogenation and hydration.

Small metal particles dispersed in the micropores of acidic zeolites are essential to important heterogeneous catalytic processes. An important example is the use of such catalysts in the hydro-isomerisation reaction of alkanes.[1] Whereas the bifunctional nature of the reaction mechanism[2,3] is well understood, the interaction between metal particle and zeolitic proton is poorly understood. Spectroscopic data, summarised by Gallerot[4] indicate that the small metal particles near zeolite cations or protons are electron deficient. However, the possibility of transfer of electrons to the non-reducible zeolite is difficult to accept.

Quantum chemical calculations[5,6] of metal particles located next to cations demonstrated that spectroscopic data could be interpreted as polarisation of small metal particles.

Sachtler and Zhang[7] proposed that metal atoms next to zeolitic protons are chemically changed since, at increased temperature, proton exchange between zeolite and metal particle may occur.

Here we present a quantum chemical study of this proton-exchange reaction. A model description of a palladium atom in contact with a zeolite cluster is used. The cluster approximation to represent zeolites has been widely explored.[8] In combination with the use of density functional theory (DFT) based electronic structure codes and full geometry optimisation, protonation energies can be reproduced with an accuracy of *ca.* 20 kJ mol^{-1}. Not only interaction energies, but also the changes in IR frequency of the proton as well as chemisorbed CO will be discussed. To analyse chemistry intrinsic to the Pd–H^+ system we have also studied the reaction energy diagrams of CO hydrogenation and hydration. It appears that proton transfer dramatically affects these reactions.

Our work is to be compared with earlier work by Yakovlev and co-workers,[9,10] who analysed the interaction of small Pd_4 and Pd_6 clusters with a proton, without explicit consideration of the zeolitic lattice.[9] In a second study, the platinum atom interaction with a zeolitic cluster was studied, however, to date, the protolysis reaction has not been considered explicitly.

Computational details

The calculations are based on DFT[11,12] as implemented in the DGAUSS program (version 3.0) produced by Cray.[13] A generalized gradient approximation to the exchange

(Becke[14]) and correlation (Lee *et al.*[15]) was used, and applied self-consistently. The calculated energies are without zero-point energy corrections, because of the large additional computational cost needed to calculate the frequencies.

The basis sets used are of double-zeta quality and include polarisation functions for all atoms (DZVP2).[16] They were optimised for use in DF calculations in order to minimise the basis set superposition error (BSSE).[17] A second set of basis functions, the fitting basis set, is used to expand the electron density in a set of single-particle Gaussian-type functions. A pseudopotential basis set was used for palladium. This pseudopotential basis set includes relativistic effects for heavy atoms.[18]

Several clusters of different sizes are used to model the acidic zeolite. The first, $H_3SiOHAl(OH)_2OSiH_3$, named the 3TOH cluster for easier reference, was used for most of the work. The adsorption position of the palladium atom was checked on $H_3SiOHAlOH(OSiH_3)_2$, the 4TOH cluster. The adsorption and reduction of the palladium ion was analysed on a 4TH ring cluster (see Fig. 2, later). The short names represent the number of tetrahedral (T) atoms in the cluster and the 'H' or 'OH' refers to the kind of termination on the aluminium atom, hydrogen atoms or hydroxy groups, respectively. The peripheral bonds of the silicon atoms were saturated with hydrogen atoms in all clusters. No symmetry or geometry constraints have been imposed in any of the structures studied.

The adsorption geometry of the palladium atom is studied on three different models of the acidic zeolite, respectively, the 3TOH cluster, the 4TOH cluster, and the 4TH ring cluster doubly substituted with aluminium atoms. For all these models the adsorption energies of the palladium atom on the acidic zeolite are compared. We also computed the IR frequencies of the OH-stretching vibrations and the deprotonation energies of the zeolite cluster models.

The reduction of the palladium ion by hydrogen on an acidic zeolite is modelled on the 4TH cluster.

The protolysis reaction is studied on the 3TOH model of the zeolite. The interaction of the palladium atom on the 3TOH model with a CO molecule is studied with and without proton transfer. The IR frequencies of the CO-stretching vibration are calculated for the bare molecule, the free PdCO cluster, PdCO on the acidic 3TOH model, and CO on the protonated Pd on the 3TOH model.

The catalytic reaction cycle to produce formaldehyde from hydrogen and carbon monoxide is studied on the 3TOH model of the zeolite. The energy changes of the elementary reaction steps are calculated.

The catalytic reaction cycle to produce formic acid from water and carbon monoxide is studied on the 3TOH model of the zeolite. The energy changes of the elementary reaction steps are calculated.

Results and Discussion

Adsorption geometry of a palladium atom on an acidic zeolite cluster

The preferred adsorption position of a palladium atom is in a two-fold position between the proton and an oxygen atom, as shown in Fig. 1. The elongation of the OH bond length shows that there is a bonding interaction between the palladium atom and the proton. The palladium atom is also tightly bonded to an oxygen atom. The nature of this interaction follows from the lengthening of the other two bonds of this oxygen to the silicon and the aluminium. Bonding of a palladium in a three-fold position with two oxygen atoms and a proton, as shown in Fig. 1(c), is energetically less favourable than the two-fold position on the same 4TOH cluster, Fig. 1(d). The adsorption energies are given in Table 1. The energy difference for the two-fold position on the 3TOH and 4TOH clusters is negligible. The three-fold position has an energy that is *ca.* 20 kJ

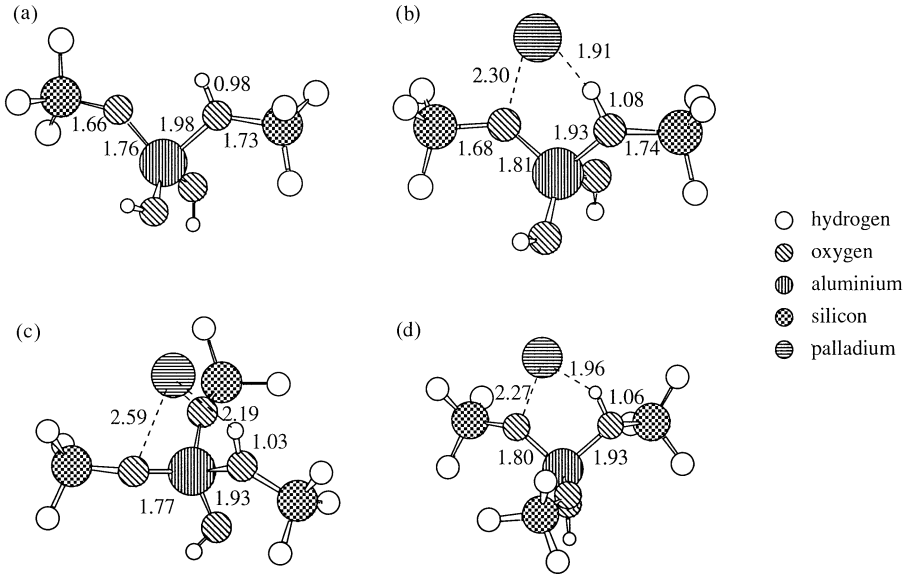

Fig. 1 Adsorption of palladium atom onto a zeolitic proton site. (a) 3TOH cluster without palladium; (b) palladium adsorbed on a 3TOH cluster; (c) palladium adsorbed on a 4TOH cluster in a three-fold coordination; and (d) palladium adsorbed on a 4TOH cluster in a two-fold coordination. All distances are given in Å.

higher. Another possible type of binding would be the interaction of a palladium atom with two protons on a doubly substituted ring, Fig. 2(c). However, this configuration is also found to be less stable than the two-fold adsorption position.

The calculated deprotonation energy of the 3TOH cluster is slightly higher than the experimental deprotonation energy of ZSM5,[19] as is shown in Table 2. The computed energy differences for proton transfer, as for instance discussed in the next two sections,

Table 1 Adsorption energies of a palladium atom on various models of zeolite

	adsorption energy/kJ mol^{-1}
Pd on 3TOH	−58.6
Pd on 4TOH in a two-fold coordination	−55.0
Pd on 4TOH in a three-fold coordination	−34.4

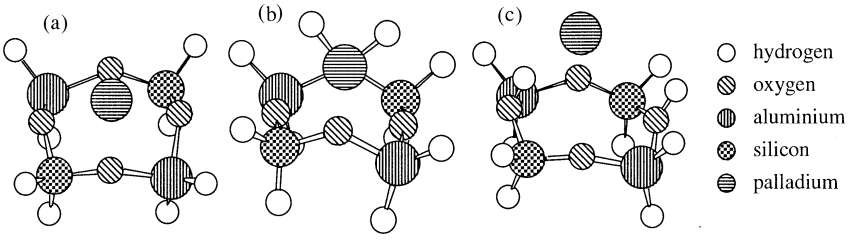

Fig. 2 Adsorption to a doubly substituted 4TH ring cluster. (a) Pd^{2+}; (b) dissociatively adsorbed hydrogen on Pd^{2+}; (c) palladium atom in a two-fold adsorption position.

Table 2 Deprotonation energy of an acidic site in a zeolite

	deprotonation energy/kJ mol^{-1}
calculated	1305
experimental	1250

are expected to have an error <55 kJ mol^{-1} because the stronger proton binding is compensated for by increased interaction with the palladium atom or ion.

As shown in Table 3 the harmonic stretching frequency of the OH bond is redshifted by *ca.* 1400 wavenumbers to the red of the spectrum. This illustrates the strong hydrogen-bonding interaction of the palladium atom with the zeolitic proton. The value for the downward-shifted harmonic stretching-frequency of the OH group is given in a range of wavenumbers, because it is broadened. The large downward shift indicates that the palladium atom acts as a strong base and is consistent with the loss in observed[7] IR intensity from large additional broadening effects.[20]

Adsorption geometry of a palladium ion adsorbed onto a zeolite cluster

The cluster model used for the reduction of a palladium ion by hydrogen is given in Fig. 2, this is a doubly aluminium-substituted four-ring. The energies involved are 68.9 kJ for

Table 3 Harmonic stretching frequency of the acidic OH with and without an adsorbed palladium atom

	OH_s (harmonic)/cm^{-1}
free hydroxy group	3664
hydroxy group with adsorbed Pd	2142–2229

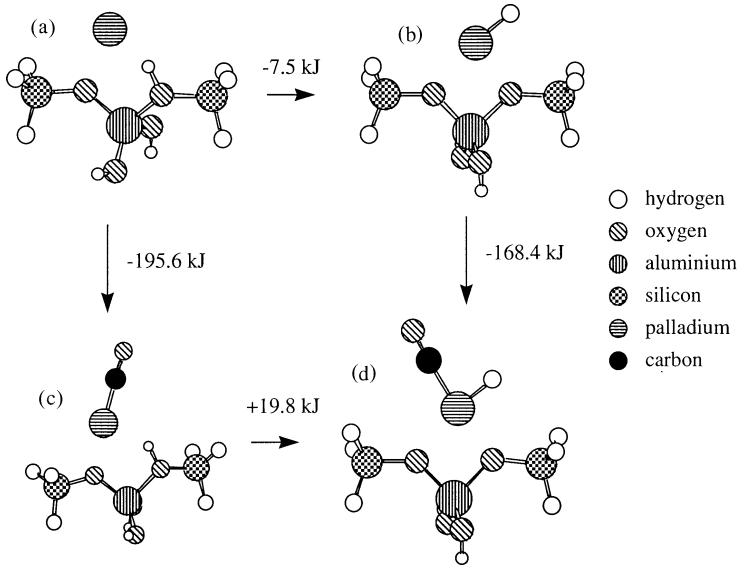

Fig. 3 Adsorption of CO onto a palladium atom and protonated palladium atom. (a) Palladium adsorbed on an acidic site; (b) protonated palladium adsorbed on a basic site; (c) CO adsorbed onto the palladium atom; (d) CO adsorbed onto protonated palladium.

Table 4 Computed harmonic stretching frequencies of carbon monoxide on various substrates

	CO_s harmonic/cm^{-1}
PdCO	1986
PdCO on 3TOH	2010
protonated PdCO on 3TO	2069
free CO	2084

dissociative endothermic adsorption of hydrogen to the palladium ion. The reduction of the palladium ion to palladium atom and the transfer of two protons to the zeolite is an exothermic step with an energy of −187.5 kJ. The overall reaction energy of the reduction of palladium ions by hydrogen is exothermic and is calculated to be −119 kJ mol^{-1}.

Protolysis of the palladium atom and CO adsorption

The protolysis reaction is studied with the 3TOH model of the zeolite. In Fig. 3 the protolysis reaction is shown in combination with the adsorption of carbon monoxide. The energy difference between protonated Pd($PdH^+—Z^-$) and hydrogen-bonded Pd (Pd—HZ) is only −7.5 kJ. Hence, the protolysis reaction is thermodynamically possible.

The IR frequency of the CO-stretching vibration of a CO molecule adsorbed onto a free palladium atom is compared with that of CO adsorbed onto a palladium atom next to an acidic site, in Table 4. Protonation of the palladium atom shifts the IR frequency of the CO stretch to the blue even more than CO adsorbed onto the unprotonated

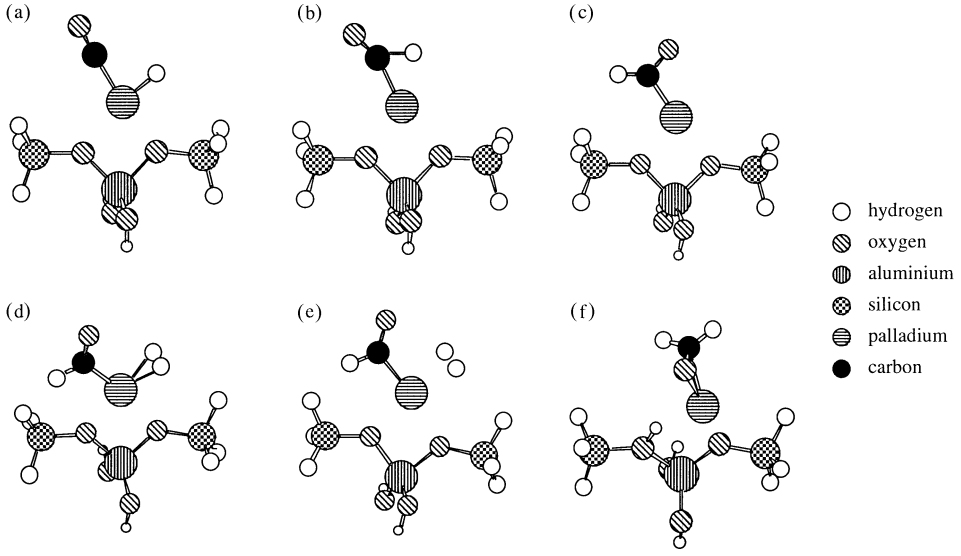

Fig. 4 Reaction intermediates of formaldehyde formation. (a) CO adsorption on PDH^-Z^+; (b) insertion of hydrogen atom onto the M—C bond; (c) adsorbed formyl; (d) H_2 adsorption; (e) H_2 rotation; (f) formaldehyde formation and proton back-donation.

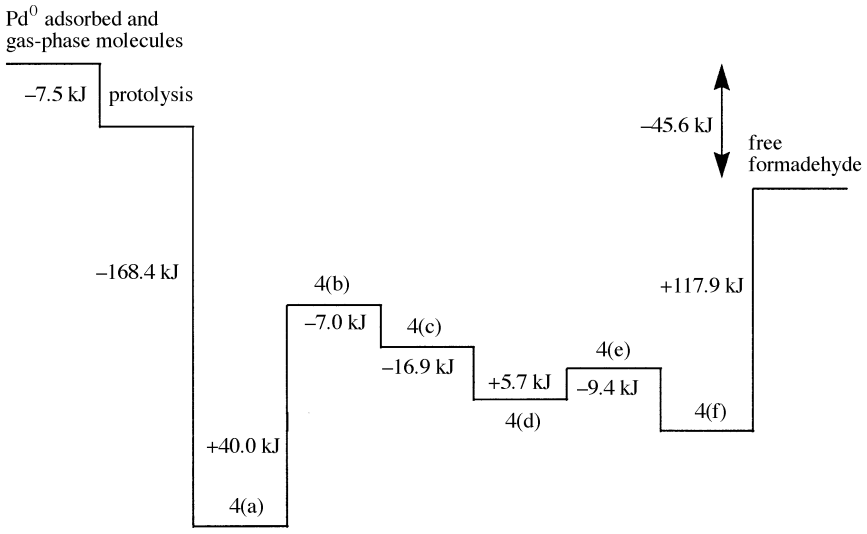

Fig. 5 Reaction energy diagram for formaldehyde formation

palladium. This agrees with the concept of electron deficiency of palladium. Calculated results indicate that protolysis is consistent with experimental observations.[21] It has also been shown[22] that there is increased intensity in the HO_s vibration on the original non-shifted position upon adsorption of CO. Hence, the proton is transferred back to the zeolite when CO is adsorbed. This is consistent with the endothermicity of the proton transfer reaction in the presence of chemisorbed CO (Fig. 3).

Catalytic reaction cycle of the H_2 and CO reaction to formaldehyde

Fig. 4 and 5 show the reaction intermediates and their corresponding energies for the CO hydrogenation reaction. In intermediate states (a)–(d), Pd is formally in the Pd^{2+} state. It only only reduced on formaldehyde formation (f) accompanied by proton back-donation to the zeolite lattice. It is this proton back-donation that makes the formaldehyde formation exothermic.

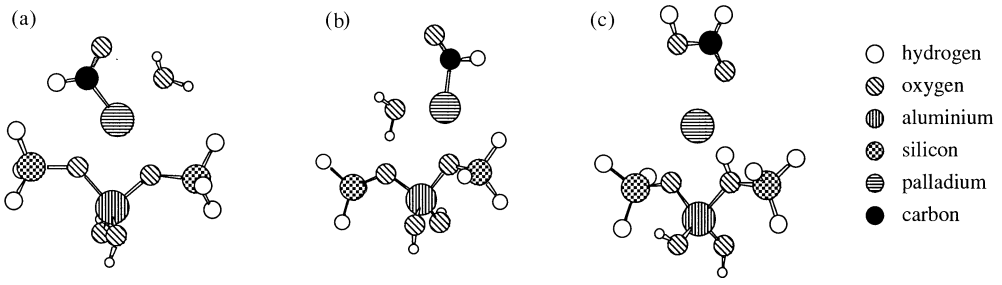

Fig. 6 Reaction intermediates of formic acid formation. (a) Water adsorption onto Pd^{2+}; (b) water adsorption onto basic zeolite oxygen; (c) formic acid formation by OH insertion and proton back-donation.

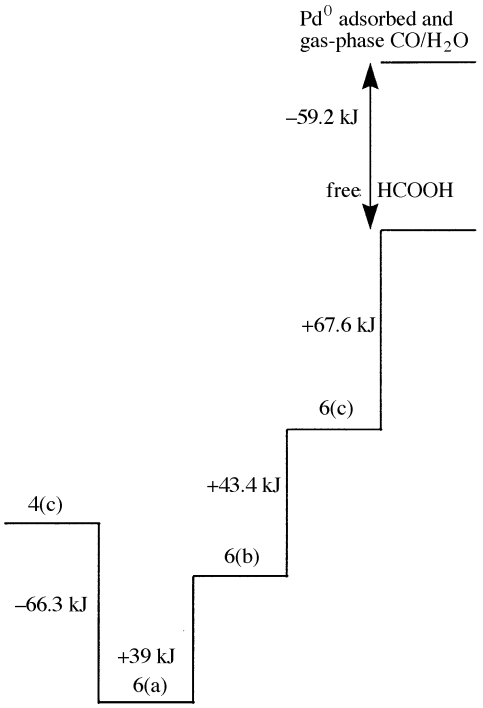

Fig. 7 Reaction energy diagram for formic acid formation

We can consider H_2 dissociation in this case to be a heterolytic process, formally generating H^- and H^+ ions. We have seen, in previous sections, that reduction of Pd^{2+} is very exothermic. The calculations indicate that the elementary reaction step for formyl formation is the most unfavourable, apart from desorption of the aldehyde. Because of the gain in entropy upon desorption one expects the latter to occur readily at higher temperatures. The results found are consistent with Driessen *et al.*'s [23] proposal that Pd^{2+} ions are favourable candidates for methanol formation on supported catalysts.

Catalytic reaction cycle of the H_2O and CO reaction to formic acid

Fig. 6 and 7 represent the intermediates and the reaction energy diagram corresponding to the formation of formic acid from CO and water. The reaction energy diagram starts with the energy of structure Fig. 4(c), the adsorbed formyl. In contrast to the previous case, formic acid formation from adsorbed formyl and water is thermodynamically unfavourable. Again the reaction proceeds such that Pd^{2+} is reduced to Pd^0, which is less favourable in this case, since it is due to heterolytic splitting of water. Nonetheless, the endothermicity of the reaction is relatively low and the reaction should be possible under mild conditions. Clearly, the catalytic effect of the zeolite is to act as an accepting basic site for the water proton

Conclusions

The cluster approach provides useful data to support mechanistic models of the metal atom–proton adducts in zeolites. The palladium atom has to be considered as a strong

base that can be readily protonated. Its formal valency then changes to 2+. The palladium atom–proton adduct system may be an interesting catalytic system. The basic nature of the zeolite oxygen atoms means that they can act as proton acceptors and hence catalyse reactions requiring heterolytic cission of protonic molecules.

The authors are grateful to Dr N. I. Jaeger and Dr G. Schulz-Ekloff for many fruitful discussions. Financial support from the DFG (AZ 436 CSR 113-11) and NCF (96.5284) is gratefully acknowledged.

References

1 J. A. Moulijn, R. A. Sheldon, H. van Bekkum and P. W. N. H. van Leeuwen in *Catalysis, an Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, ed. J. A. Moulijn, P. W. N. M. van Leeuwen and R. A. van Santen, Elseiver, Amsterdam, 1995, p. 33.
2 G. A. Mills, H. Heinemann, T. H. Milliken and A. G. Oblad, *Ind. Eng. Chem.*, 1953, **45**, 134.
3 P. Weisz, *Adv. Catal.*, 1962, **13**, 137.
4 P. Gallerot, *Catal. Rev.-Sci. Eng.*, 1979, **20**, 121.
5 E. Sanchez Marcos, A. P. J. Jansen and R. A. van Santen, *Chem. Phys. Lett.*, 1990, **167**, 399.
6 A. P. J. Jansen, R. A. van Santen, *J. Phys. Chem.*, 1990, **94**, 6764.
7 W. M. H. Sachtler and Z. Zhang, *Adv. Catal.*, 1993, **39**, 129.
8 R. A. van Santen, in *Chemisorption and Reactivity on Supported Clusters and Thin Films*, ed. R. M. Lambert and G. Pacchioni, Kluwer, Dordrecht, 1997, p. 371.
9 A. L. Yakovlev, G. M. Zhidomirov, K. M. Neyman, V. A. Nasluzov and N. Rösch, *Ber. Bunsen-Ges. Phys. Chem.*, 1996, **100**, 413.
10 A. L. Yakovlev, K. M. Neyman, G. M. Zhiodomirov and N. Rösch, *J. Phys. Chem.*, 1996, **100**, 3482.
11 P. Hohenberg and W. Kohn, *Phys. Rev. B*, 1964, **136**, 864.
12 W. Kohn and L. J. Sham, *Phys. Rev. B*, 1965, **140**, 1133.
13 J. Andzelm and E. Wimmer, *J. Chem. Phys.*, 1992, **96**, 1280.
14 A. D. Becke, *J. Chem. Phys.*, 1986, **84**, 4524.
15 C. Lee, R. G. Parr and W. Yang, *Phys. Rev. B*, 1988, **37**, 785.
16 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.
17 J. Sauer, *Chem. Rev.*, 1989, **89**, 199.
18 H. Chen, M. Krasowski and G. Fitzgerald, *J. Chem. Phys.*, 1993, **98**, 8710.
19 E. A. Paulshtis and E. N. Yurchenko, *Russ. Chem. Rev.*, 1983, **52**, 242.
20 R. A. van Santen and G. J. Kramer, *Chem. Rev.*, 1985, **95**, 637.
21 L. L. Sheu, H. Knözinger and W. M. H. Sachtler, *J. Am. Chem. Soc.*, 1989, **111**, 8125.
22 Z. Zhang, T. Wong and W. M. H. Sachtler, *J. Catal.*, 1991, **128**, 13.
23 J. M. Driessen, E. K. Poels, J. P. Hindermann and V. Ponec, *J. Catal.*, 1983, **82**, 26.

Paper 7/01789H; *Received* 14*th March*, 1997