Catalysis Today 154 (2010) 113–117

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Surface science as a tool for probing nanocatalysis phenomena

C.P. Vinod

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, United Kingdom

ARTICLE INFO

Article history:
Available online 14 April 2010

Dedicated to Prof. B.E. Nieuwenhuys on the occasion of his retirement.

Keywords:
Steps and kinks
Defects
X-ray photoelectron spectroscopy (XPS)
Structure sensitive reactions
Nanocatalysis

ABSTRACT

Molecular level understanding of catalysis is fundamental to solve many problems related to activity, selectivity and a host of other issues. Over the years surface science techniques have been instrumental in shedding light into some of these fundamental questions. With the rapid advancement of instrumentation and microscopy techniques, the field of nanotechnology has taken unprecedented dimensions. Catalysis by nanoscale materials is an area, which has benefited most from this. A major area in nanocatalysis is aimed at identifying critical size and shape dependence of these materials towards various reactions of industrial importance. This article is aimed at looking at recent developments in the field of nanocatalysis along with the role of surface science towards understanding the role of active sites in catalysis.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The properties of 'divided metals', a word coined by Faraday, have been known to mankind for several centuries [1]. The use of colloidal gold in medical treatments like dipsomania, arthritis and in the field of ceramics as a dye material has a history dating back to several centuries. Over the last two decades, materials science researchers have been captivated by the exploration of the size dependent properties of nanoscale materials [2,3]. The discovery of powerful microscopes like scanning probe microscopy and sub-angstrom resolution transmission electron microscopy (TEM), which can give atomic and molecular level detail of the material under consideration, has given a new impetus to the field of nanoscience.

The optical and electronic properties of metal nanoparticles have been an area of intense research for physicists and chemists. Manifestations of properties exhibited due to quantum size confinements including the non-metallcity associated with metal particles on size reduction [4], tuning of the HOMO–LUMO band gap of semiconductor nanoparticles [5] and variation in the melting temperature of metal clusters [6] are all manifestations of properties exhibited due to quantum size confinements.

From a chemical perspective, the most exciting discoveries that have emerged are in the field of catalysis. Tiny metal particles are shown to exhibit a reactivity that is significantly different when compared with their bulk counterpart. The best example to date is observed in catalysis by gold, in which gold shows no reactivity in the bulk phase [7], but then becomes a superior catalyst in a nanoregime [8–10]. Decreasing particle size to the nanometer range increases the dispersion and hence increases the surface area on which the reaction is carried out. The concentration of low coordinated sites (defect sites) is relatively abundant in nanomaterials. These sites usually provide sites of low activation barrier for reactant molecule [11]. More importantly, they provide sites of low activation barrier for reactant molecules, which are otherwise negligible or absent in bulk systems.

One of the principal goals of modern day catalysis research is to have further control over activity, selectivity and specificity of catalytic systems [12,13]. This can be achieved in various ways, including: (i) selection of the catalyst material and composition; (ii) manipulation of the atomic structure, morphology and shape of the catalyst; and (iii) choice of the support. Determining active phases/sites in catalysis is central to all these problems in order to design smart and robust catalysts.

2. Size and shape effects in catalysis

Catalysis is known as a surface phenomenon, where the reaction occurs on the large fraction of exposed atoms. Thus, a catalyst is typically only a few nanometers in size dispersed on a suitable support. Since surface to volume ratio increases with size reduction, it is intuitive to argue that the smaller the size of the catalyst particle, the better it should perform. The actual reactivity pattern with size is, however, a little more complicated than this simple assumption. Unlike the common scenario in catalysis, in which the catalytic performance scales with the surface to volume ratio of the dispersed catalyst, nanocatalysts are distinguished by their unique

---

E-mail address: cpvinod@gmail.com.

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.018

and non-scalable properties that originate from the highly reduced dimensions of the active catalytic aggregates.

Surface spectroscopy has been an indispensable tool for studying nanomaterials for several years. Early surface science studies were performed by looking at the reactivity of vacuum evaporated metal clusters deposited on suitable supports. X-ray photoelectron spectroscopy (XPS), a surface sensitive technique, is a powerful tool for probing the reactivity and electronic structure of these materials. For example, an XPS investigation on the reactivity of oxygen towards Ag nanoparticles was found to be markedly different from bulk Ag: the nanoparticles were able to produce atomic oxygen at 80 K [14]. The dissociation of CO on small Ni clusters observed using XPS also indicated that the reactivity of small clusters is indeed different from the bulk [15]. Similarly, dissociation of H_2S on Ni has strong size dependence [16].

Cobalt catalyst, used in the Fischer–Tropsch (FT) synthesis, is a relevant example that shows particle size dependent reactivity. From turn over frequency (TOF) measurements, it is reported that the Co particles in the size range 6–200 nm do not exhibit any size dependence, with particles less than 6 nm showing poor activity [17–19]. The origin of size dependence in Co FT catalysis is addressed by de Jong and co-workers recently [20]. The NO–CO reaction carried out using a pulsed molecular beam on a model Pd/MgO(1 0 0) catalyst with three different sizes (2.8, 6.9 and 15.6 nm) showed that the catalyst with the biggest particle size, which predominantly exposes the (1 0 0) surface, was least active. The other two catalysts expose (1 1 1) facets: the catalyst with 6.9 nm particles was found to be more active than the one with 2.8 nm particles. The strongly bound N atoms (formed on the low coordinated sites on small clusters) decreased the available sites for NO dissociation, leading to decreased catalytic activity [21]. The interaction of Ag clusters supported on HOPG showed a dissociative adsorption of $CHCl_3$, which decreased sharply with increasing size [22].

Developments in the field of optics and cluster generation sources show that it is possible to produce size-selected clusters and deposit them onto a suitable substrate [23–25]. Molecular clusters deposited on suitable oxide substrates form monodispersed catalytic model systems for the study of industrially relevant reactions, where selectivity can be controlled via atom-by-atom precision. Several groups have studied the reactivity of such clusters for understanding the critical size dependence of chemical reactivity on various supports.

Heiz and co-workers carried out a systematic study of atom-by-atom dependence on the product selectivity of acetylene polymerization on size-selected Pd clusters. They have found that selectivity for benzene formation is 100% for tiny clusters with 2–3 atoms. The other products, such as butadiene and butene are catalyzed to different degrees for clusters that have 20–25 atoms (see Fig. 1) [26].

The last several years has seen an enormous interest in catalysis by gold. Bulk gold, which is catalytically inactive, turns out to be an excellent catalyst in the size regimes 3–5 nm. The origin of catalysis by gold is thoroughly debated in the literature. There are excellent reviews available in this field to the interested reader, but this is beyond the scope of this article [27,28].

It is clear that size dependence in catalysis is much more complex than what initial hypothesis suggest and there is no single theory that can explain all the phenomena observed. It is believed that the surface atoms or a combination of surface atoms should possess certain 'geometries' with required 'electronic' properties which will enable the surface to act as an efficient catalyst [29,30]. Electronic (ligand) effects indicate the nature and strength of the bond between the d-band orbital of the surface atom, and the molecular orbitals of the reactants and the products. The surface atoms in different environments have different local electronic structures and interact differently with adsorbate molecules. In general, the d-band center, which is the first moment of the density of states, projected against the d-orbitals for the surface atoms interacting with the adsorbates as a reactivity descriptor. Transition metal surface with open surface and low coordination number atoms (like steps, edges, kinks and corners) have higher lying d-states and tend to interact strongly with adsorbates. Geometric effects result in a minimum ensemble of atoms with a specific arrangement for adsorption and for the reaction to take place. Nanoparticles of various morphologies and sizes possess different edge and vertex atoms, and fractions of different crystallographic orientations. Furthermore, these nanoparticles show different activities in structure sensitive reactions. Fig. 2 summarizes how the structure sensitivity can be correlated with turn over frequency (TOF). If the entire nanoparticle surface possesses necessary properties for catalyzing a reaction then the TOF will remain constant with varying sizes and shapes (curve A). Such reactions are considered to be structure insensitive or intrinsically size/shape independent. However, it is not always the case that all the atoms constitute the active site. The TOF of such reactions depend on the

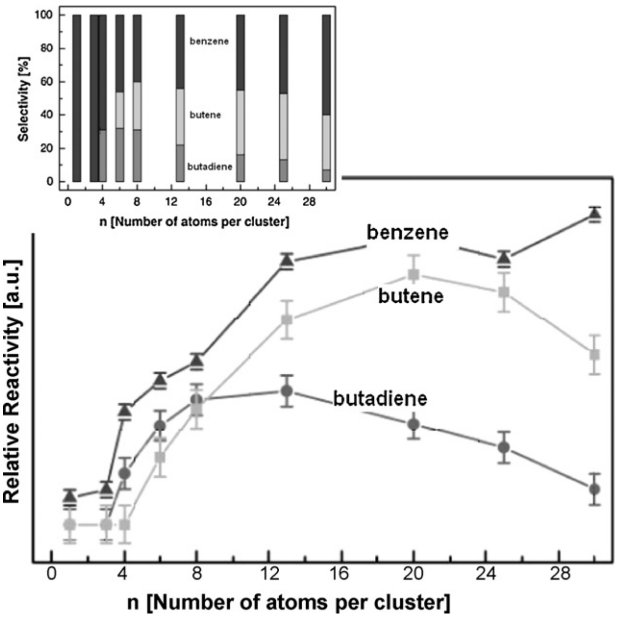

Fig. 1. Atom-by-atom dependence of Pd clusters for acetylene polymerization. Inset shows the selectivity for the reaction towards the number of Pd atoms (adapted from Ref. [26]).

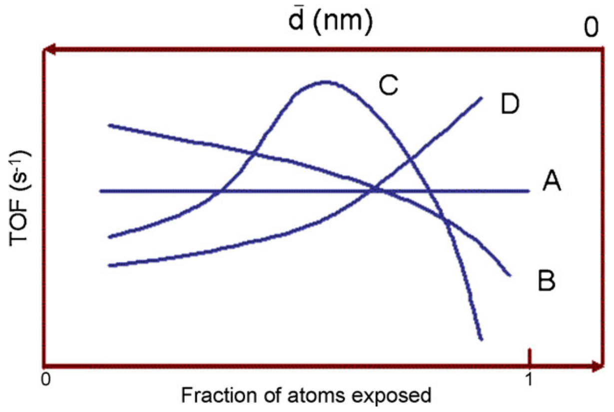

Fig. 2. Variation of turn over frequency with particle size and fraction of the atoms exposed for structure insensitive reaction (curve A) and structure sensitive reactions (B–D) (adapted from Ref. [31]).

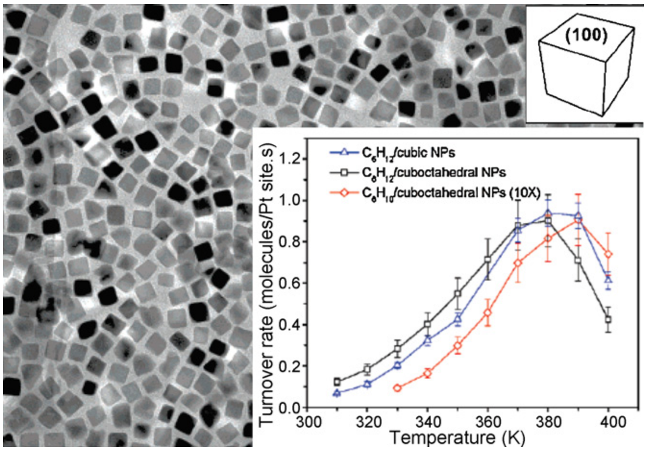

Fig. 3. TEM image of cubic Pt nanoparticle (average particle size 12 nm). The inset shows the selectivity for benzene hydrogenation on cubic and cuboctahedral particles (adapted from Ref. [34]).

size and shape of the nanoparticle and are considered structure sensitive reactions.

It is clear from Fig. 2 that structure can influence a reaction in different ways. If the TOF decreases with increasing particle size, then it is called negative particle size effect or antipathetic size dependence (curve B). Positive particle size effect is when the TOF increases with decreasing particle size, as depicted by curve D. In certain cases the TOF goes through a maximum where small particles exhibit negative size effects and larger particles a positive size effect (curve C). This would imply that, apart from size, the shape of the particle would play a very crucial role in determining the selectivity, stability and activity of the catalyst.

The study of shape effects in nanocatalysis has been increasing in prominence in recent years. This is mainly due to the new synthetic strategies developed in colloidal metal nanoparticle preparation over the last few years [32,33]. The possibility of making monodispersed particles with precise size and shape control exposing distinct crystallographic faces opens up excellent avenues for nanocatalysis. Recently, Somorjai and co-workers studied benzene hydrogenation selectivity over Pt nanoparticles of different shapes. They found high selectivity for cyclohexane on a cubic nanoparticle that has predominantly (1 0 0) faces, compared with the selectivity over a cuboctahedral particle, which has both (1 1 1) and (1 0 0) faces, and which produced both cyclohexene and cyclohexane [34] (see Fig. 3). Pyrrole hydrogenation on Pt nanocubes showed significant selectivity towards *n*-butylamine compared with Pt polyhedral nanoparticles [35]. Catalytic oxidation of styrene on silver nanoparticles also shows major sensitivity towards (1 0 0) dominated nanocubes in comparison with spherical or truncated triangular particles [36].

3. Origin of catalysis at the nanoscale probed by surface science techniques

As mentioned in the previous section, the origin of catalysis at the nanoscale could be attributed to the electronic and geometric factors accompanying the size reduction of nanoparticles. As the size of the material shrinks, the valence band becomes sharper with a decrease in the density of states (DOS) at the Fermi level. As a result there are more localised electrons and so the nanoparticles lie between such molecules that have discrete energy levels and bulk metal that have continuous energy bands.

The change in electronic structure associated with size reduction has been probed by several surface science methods [37,38]. The shift in core level binding energy accompanying size reduction in nanoparticles compared to bulk (CLBS) can often be measured with XPS. Such positive core level shifts with decreasing particle size can be explained by a combination of initial and final state effects: with decreasing mean particle diameter, the screening efficiency of the core–hole state created by the photoionization process decreases, leading to a positive core level shift [39,40]. In literature, such positive shifts in core level binding energy have been attributed to a transition from metallic to non-metallic state [41,42].

The core level binding energy of the metal nanoparticle with size reduction has been extensively studied by XPS in relation to catalysis [43–46]. The dependence of particles size on stabilization of different oxygen species and their role have been looked into by employing XPS on ethylene epoxidation over Ag clusters [45]. The hydrogenation of vinyl acetylene by supported Pd nanoparticles shows a drastic increase in reaction rate for smaller sized nanoparticles. A direct correlation between the shifts in Pd($3d^{5/2}$) core level with rate has been observed and the enhanced rate is attributed to the modified electronic structure [46].

Nanoscale catalysis by gold has been thoroughly debated in the literature [27]. One of the earlier studies used STM as a tool for probing the electronic structure of tiny gold clusters on TiO_2 in relation to catalytic oxidation of CO [47]. The strong size dependence of ~3 nm clusters was attributed to the onset of a metal–non-metal transition. There are reasons apart from electronic structure, which have been proposed for the reactivity of gold nanoparticles. Special sites on the nanoparticles, metal support interactions, etc. are worth mentioning [28].

There are a number of models that have been proposed as to why nanoparticles are more active than their bulk counterpart. Notably, the model proposed by Van Hardeveld and Hartog several years ago is still widely appreciated [48]. This is based on coordinatively unsaturated atoms and B5 sites present on the surface in reduced dimensions. The role of these special sites in reactivity of small Ni, Pd and Pt particles with sizes between 1.5 and 7 nm has been investigated. These results showed that smaller particles have a stronger interaction with N_2 and some other adsorbed molecules than larger particles [49]. It is worth mentioning that the concept of low coordinated sites on stepped surfaces and their significantly different reactivities were proposed by Taylor in the 1920s [50].

Identifying and selectively probing special sites in a catalyst is one of the most challenging problems far from fundamental reasons. Designing new materials, improving selectivity and activity all rely on this key concept. Studies on well-defined single crystals are a fairly straightforward approach to probe these sites. In the late 1970s, the molecular beam experiments on HD exchange reaction studied on a stepped Pt single crystal surface indicated that reactivity is markedly different when the reactants approach the open side of the steps [51]. This provided a surface geometry where the reactive step sites being readily accessible to the incoming molecules from the gas phase for reaction. The reactivity decreased by a factor of two when the inner corners of the steps were shadowed. Infrared reflection absorption spectroscopy (IRAS) experiments carried out on the interaction of CO and N_2 on stepped Pt surface also showed a preferential adsorption on steps than the terrace sites [52,53]. One of the possible ways to identify these sites is to selectively block them and compare the reactivity with a clean surface [54,55]. The N_2 dissociation on a stepped Ru(0 0 0 1) surface demonstrated such an example. The rate of N_2 dissociation was found to decrease by 7 orders of magnitude by selectively blocking steps by Au deposition (Fig. 4). Similarly, dissociation of CO on a stepped Ni(14 13 13) surface was found to be dominated by the presence of these special sites [55]. A surface covered with 0.05 ML of S is found to completely suppress the dissociation of CO. The first microscopic evidence to prove that the dominance of step sites in reactivity came from Ertl and co-workers, who imaged NO dissoci-

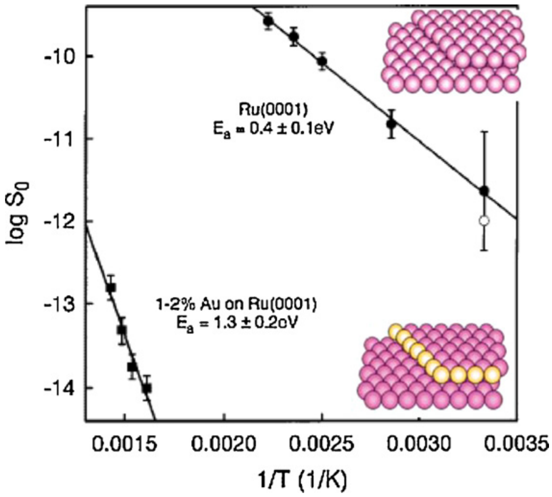

Fig. 4. Rate of N_2 dissociation on stepped Ru(0 0 0 1) surface and the steps blocked by Au (adapted from Ref. [54]).

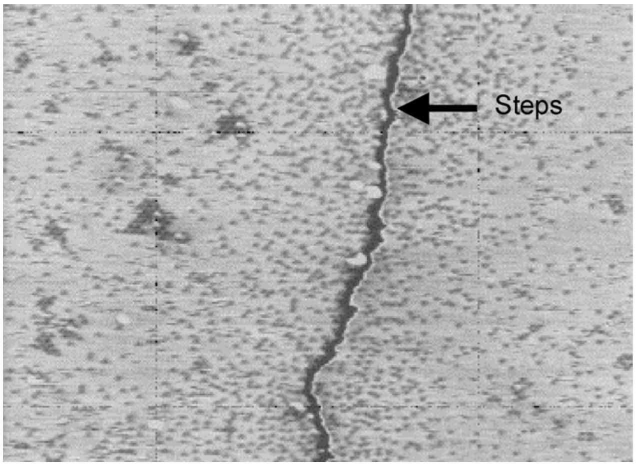

Fig. 5. STM image (∼40 × 30 nm) obtained after dosing NO at 315 K on a Ru(0 0 0 1) surface. Monoatomic step decorated by N_{ad} is shown by arrow (adapted from Ref. [56]).

ation on Ru(0 0 0 1) [56]. The STM image taken after exposing NO at 315 K clearly demonstrated that the dissociation takes place on the steps. N_{ad} formed during the decomposition decorated the steps with O_{ad} atoms rapidly diffusing to the terrace sites (see Fig. 5).

Recently, it was shown by Nieuwenhuys and co-workers that the decomposition of several small molecules on a well-defined gold surface is dominated by steps [57,58]. A stepped Au(3 1 0) surface is found to decompose NO at low temperatures, producing N_2O and O_{ad} on the surface. The XPS spectra obtained after dosing NO at 80 K clearly showed the presence of N_2O on the surface produced by the decomposition (see Fig. 6). The lower binding energy species at 401.5 eV in the N1s spectra is assigned to N_2O formed by decomposition of NO. The inset of the figure shows the corresponding O1s spectra at 160 K, which shows two distinct oxygen species produced during the decomposition of NO. The same surface was able to activate O–H bonds in methanol producing methoxy species on the surface (see Fig. 7). The surface warmed to 200 K after dosing methanol at 80 K showed molecular methanol, methoxy species and CH_x fragments on the surface. These results are interesting because other closed surfaces of gold are not able to drive the decomposition chemistry. Recently, the adsorption of CO was carried out on the same surface and was studied by employing synchrotron XPS. This showed that there was preferential adsorption of CO onto the step sites [59]. These results clearly demonstrate the role played by defects in gold chemistry, and it is probable that this has direct implications on the nanocatalytic behaviour that is exhibited by this metal.

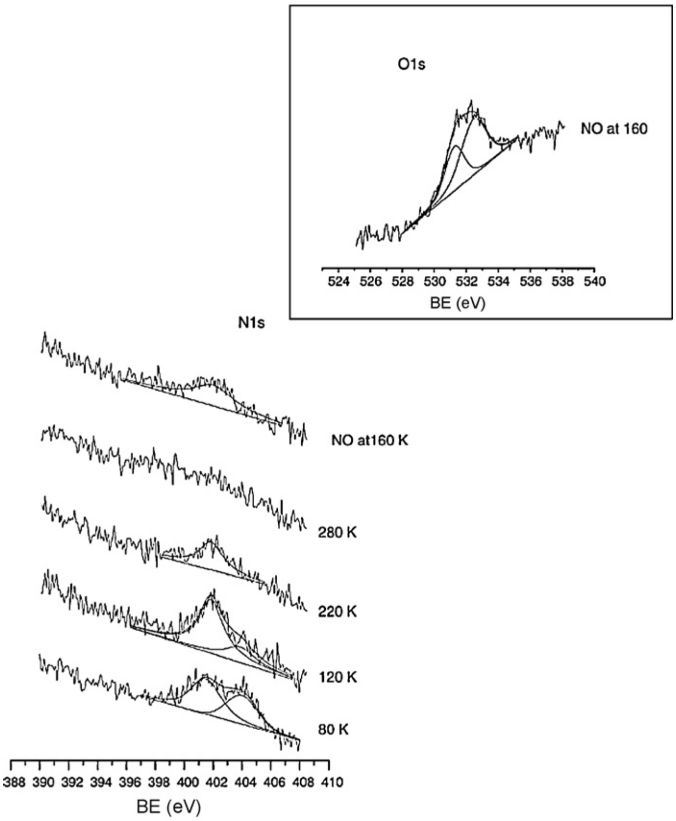

Fig. 6. N1s and O1s XP spectra obtained by dosing NO at 80 K (∼10^{-6} mbar, 30 min) and progressively warming to room temperature. Inset shows the O1s spectra obtained by dosing NO at 160 K (adapted from Ref. [57]).

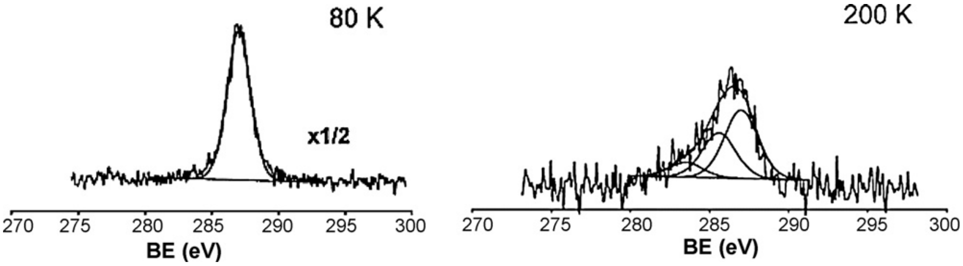

Fig. 7. C1s XPS spectra obtained by dosing 2 L of CH_3OH on Au(3 1 0) at 80 K followed by warming the surface to 200 K (adapted from Ref. [58]).

4. Conclusions and outlook

Catalysis by nanoscale materials is still evolving and clearly represents a solution for many industrial applications. Surface science techniques and synthetic methodologies for making nanomaterials with specific sizes and shapes are developing at a rapid pace. Investigation from fundamental surface science studies such as identifying and selectively probing catalytically active sites by careful experiments on well-defined model systems will provide further insight into synthesising/designing/engineering tailored catalysts for desired applications with higher activity, selectivity and stability.

Acknowledgements

The author is grateful to all his teachers, past and present collaborators for their constant support and encouragement.

References

[1] M. Faraday, Philos. Trans. 147 (1857) 145.
[2] C.N.R. Rao, G.U. Kulkarni, P.J. Thomas, P.P. Edwards, Chem.-Eur. J. 8 (2002) 28.
[3] A.P. Alivisatos, J. Phys. Chem. 100 (1996) 13226.
[4] C.P. Vinod, G.U. Kulkarni, C.N.R. Rao, Chem. Phys. Lett. 289 (1998) 329.
[5] T. Vossmeyer, L. Katsikas, M. Gienig, I.G. Popovic, K. Diesner, A. Chemseddine, A. Eychmiiller, H. Weller, J. Phys. Chem. 98 (1994) 7665.
[6] Ph. Buffat, J.-P. Borel, Phys. Rev. E 13 (6) (1976) 2287.
[7] B. Hammer, J.K. Norskov, Nature 376 (1995) 238.
[8] M. Haruta, Chem. Rec. 3 (2003) 75.
[9] A.S.K. Hashmi, G.J. Hutchings, Angew. Chem. Int. Ed. 45 (2006) 7896.
[10] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.
[11] C.J. Weststrate, A. Resta, R. Westerström, E. Lundgren, A. Mikkelsen, J.N. Andersen, J. Phys. Chem. C 112 (17) (2008) 6900.
[12] J.H. Sinfelt, AIChE J. 19 (1973) 673.
[13] G.A. Somorjai, J.Y. Park, Angew. Chem. Int. Ed. 47 (2008) 9212.
[14] V.I. Bukhtiyarov, A.F. Carley, L.A. Dollard, M.W. Roberts, Surf. Sci. 381 (1997) L605.
[15] A.K. Santra, S. Ghosh, C.N.R. Rao, Langmuir 10 (1994) 3937.
[16] C.N.R. Rao, V. Vijayakrishnan, A.K. Santra, M.W.J. Prins, Angew. Chem. Int. Ed. 31 (1992) 1062.
[17] E. Iglesia, Appl. Catal. A 161 (1997) 59.
[18] G.L. Bezemer, J.H. Bitter, H.P.C.E. Kuipers, H. Oosterbeek, J.E. Holewijn, X. Xu, F. Kapteijn, A.J. Van Dillen, K.P. De Jong, J. Am. Chem. Soc. 128 (2006) 3956.
[19] A. Barbier, A. Tuel, I. Arcon, A. Kodre, G.A. Martin, J. Catal. 200 (2001) 106.
[20] J.P. den Breejen, P.B. Radstake, G.L. Bezemer, J.H. Bitter, V. Frøseth, A. Holmen, K.P. de Jong, J. Am. Chem. Soc. 131 (2009) 7197.
[21] L. Piccolo, C.R. Henry, J. Mol. Catal. A 167 (2001) 181.
[22] H. Zhang, Q. Fu, Y.Y. ao, Z. Zhang, T. Ma, D. Tan, X. Bao, Langmuir 24 (2008) 10874.
[23] D.C. Parent, S.L. Anderson, Chem. Rev. 92 (1992) 1541.
[24] S.M. Lang, D.M. Popolan, T.M. Bernhardt, Chem. Phys. Solid Surf. 12 (2007) 53.
[25] U. Heiz, W.-D. Schneider, Crit. Rev. Solid State Mater. Sci 26 (4) (2001) 251.
[26] S. Abbet, A. Sanchez, U. Heiz, W.-D. Schneider, J. Catal. 198 (2001) 122.
[27] R. Meyer, C. Lemire, Sh.K. Shaikhutdinov, H.-J. Freund, Gold Bull. 37 (2004) 72.
[28] T.V.W. Janssens, B.S. Clausen, B. Hvolbæk, H. Falsig, C.H. Christensen, T. Bligaard, J.K. Nørskov, Top. Catal. 44 (2007) 15.
[29] B. Hammer, J.K. Nørskov, Adv. Catal. 45 (2000) 71.
[30] J.K. Nørskov, T. Bligaard, A. Logadottir, S. Bahn, L.B. Hansen, M. Bollinger, H.S. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl, C.J.H. Jacobsen, J. Catal. 209 (2002) 275.
[31] M. Che, C.O. Bennett, Adv. Catal. 36 (1989) 55.
[32] A.R. Tao, S. Habas, P. Yang, Small 4 (2008) 310.
[33] Y. Sun, Y. Xia, Science 298 (2002) 2176.
[34] K.M. Bratlie, H. Lee, K. Komvopoulos, P. Yang, G.A. Somorjai, Nanoletters 7 (2007) 3097.
[35] C.-K. Tsung, J.N. Kuhn, W. Huang, C. Aliaga, L.-I. Hung, G.A. Somorjai, P. Yang, J. Am. Chem. Soc. 131 (2009) 5816–5822.
[36] R. Xu, D. Wang, J. Zhang, Y. Li, Chem. Asian J. 1 (2006) 888.
[37] M.G. Mason, Phys. Rev. B 27 (1983) 748–762.
[38] B. Richter, H. Kuhlenbeck, H.-J. Freund, P.S. Bagus, Phys. Rev. Lett. 93 (2004) 026805.
[39] G.K. Wertheim, S.B. Dicenzo, Phys. Rev. B 37 (1968) 844.
[40] M.G. Mason, in: G. Pacchionic, et al. (Eds.), Clusters Model for Surface and Bulk Phenomena, Plenum Press, New York, 1992.
[41] V. Vijayakrishnan, A. Chainani, D.D. Sarma, C.N.R. Rao, J. Phys. Chem. 96 (1992) 867.
[42] C.N.R. Rao, V. Vijayakrishnan, H.N. Aiyer, G.U. Kulkami, G.N. Subbanna, J. Phys. Chem. 97 (1993) 11157.
[43] D.C. Lim, I. Lopez-Salido, R. Dietsche, M. Bubek, Y.D. Kim, Chem. Phys. 330 (2006) 441.
[44] D.C. Lim, I. Lopez-Salido, Y.D. Kim, Surf. Sci. 598 (2005) 96–103.
[45] V.I. Bukhtiyarov, I.P. Prosvirin, R.I. Kvon, S.N. Goncharova, B.S. Balzhinimaev, J. Chem. Soc., Faraday Trans. 93 (1997) 2323.
[46] Yu.A. Ryndin, L.V. Nosova, A.I. Boronin, A.L. Chuvilin, Appl. Catal. A: Gen. 42 (1988) 131.
[47] M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647.
[48] R. Van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189.
[49] R. van Hardeveld, A. van Montfoort, Surf. Sci. 4 (1966) 396.
[50] H.S. Taylor, Proc. R. Soc. Lond. Ser. A 108 (1925) 105.
[51] M. Salmeron, R.J. Gale, G.A. Somorjai, J. Chem. Phys. 67 (1977) 5324.
[52] C.E. Tripa, T.S. Zubkov, J.T. Yates, M. Mavrikakis, J.K. Nørskov, J. Chem. Phys. 111 (1999) 8651.
[53] J. Xu, P. Henriksen, T. John, Yates Jr., J. Chem. Phys. 97 (1992).
[54] S. Dahl, A. Logadottir, R.C. Egeberg, J.H. Larsen, I. Chorkendorff, E. Tornqvist, J.K. Nørskov, Phys. Rev. Lett. 83 (1999) 1814.
[55] M.P. Andersson, F. Abild-Pedersen, I.N. Remediakis, T. Bligaard, G. Jones, J. Engbæk, O. Lytken, S. Horch, J.H. Nielsen, J. Sehested, J.R. Rostrup-Nielsen, J.K. Nørskov, I. Chorkendorff, J. Catal. 255 (2008) 6.
[56] T. Zambelli, J. Wintterlin, J. Trost, G. Ertl, Science 273 (1996) 1688.
[57] C.P. Vinod, J.W. Niemantsverdriet, B.E. Nieuwenhuys, Appl. Catal. A 291 (2005) 93.
[58] C.P. Vinod, J.W. Niemantsverdriet, B.E. Nieuwenhuys, Phys. Chem. Chem. Phys. 7 (2005) 1824.
[59] C.J. Weststrate, E. Lundgren, J.N. Andersen, E.D.L. Rienks, A.C. Gluhoi, J.W. Bakker, I.M.N. Groot, B.E. Nieuwenhuys, Surf. Sci. 603 (2009) 2152.