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SURFACE RESTRUCTURING AS A MECHANISM FOR BOND BREAKING AND CATALYTIC REACTIONS AT METAL SURFACES

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Low energy electron diffraction-surface crystallography studies indicate that the more open crystal surfaces with higher Miller index restructure more readily when clean. These investigations also uncovered the predominance of adsorbate induced restructuring of surface atoms. It is suggested that one mechanism of chemical bond breaking for adsorbate molecules is surface restructuring induced bond scission and that catalytic processes on metals can be induced by the restructuring of surface atoms around the adsorbate species. While direct experimental evidence is lacking, many of the properties of the chemisorption bond and the catalytic activity on metal surfaces can be explained by the surface restructuring model. These are a) higher activity for bond breaking on more open surfaces, b) bond breaking in narrow temperature ranges and sequentially as the temperature is increased, c) the higher surface dissociation probability of molecules with higher incident kinetic energy, and d) the structure sensitivity and insensitivity of catalytic reactions.

The classical models of the structure of solid surfaces assumed a rigid lattice that holds the surface atoms in their bulk-like equilibrium positions. Surface crystallography studies in recent years, however, revealed that the surface atoms "relax" when clean; i.e., change their equilibrium position usually by contraction perpendicular to the surface [1,2]. Simultaneously, atoms in the second layer often move outward, closer to the surface plane. The lower their coordination number, the larger the relaxation as shown by LEED studies of the more open fcc(110), bcc(111) surfaces and at atomic height steps on high Miller index stepped surfaces. Clean surfaces often "reconstruct"; i.e., surface atoms seek new equilibrium positions parallel to the surface plane as well that optimize their bonding [3].

The chemisorption of an atom or a molecule on metal surfaces causes local restructuring of surface atoms around the adsorption site as shown by recent surface crystallography studies [4]. The metal surface atoms can move outward, rotate in the surface plane or shift toward the adsorbate site in order to maximize the strength of the adsorbate-substrate bonds. The surface bond becomes similar to that in multinuclear clusters, which are good models of the surface chemical bond [5]. Again, on the more open surfaces, restructuring is more pronounced [6,4h]. This type of adsorbate induced restructuring occurs rapidly within the time scale of adsorption and it is usually reversible; the surface structure returns to its clean state upon desorption. There are, however, other adsorbate induced restructuring processes that are much slower, surface diffusion controlled and not reversible [7].

In his last paper that appeared posthumously, Simonetta [8] suggested that on small metal particles the catalytically active site is produced upon the adsorption of reactants. He based his suggestion on calculations that indicated that several structural configurations of these clusters have about the same formation energy and, therefore, these particles can readily rearrange.

In this paper we propose that one mechanism for the bond dissociation of adsorbates on metals is surface restructuring and that catalytic processes on metals can be induced by the restructuring of surface atoms around the adsorbate species. Thus, adsorbate induced restructuring and surface restructuring induced bond breaking and reactivity are due to the same process of adsorbate-surface atom chemical interaction. While direct experimental evidence for this mechanism of metal surface reactivity is lacking, many of the properties of the chemisorption bond and the catalytic activity on metal surfaces can be explained by the surface restructuring model.

There is a large body of experimental data indicating that the dissociation of diatomic molecules occurs at a lower temperature on more open transition metal surfaces where surface atoms have fewer neighbors [9]. Breaking of H–H, O=O and C=O bonds as well as N≡N bonds occurs at lower temperatures and with higher probabilities on more open or stepped Pt, Ni, Fe, and Re surfaces [10]. This is also the case for breaking of C–H and C–C bonds in organic molecules. Bond breaking also occurs in narrow temperature ranges. For example, the N≡N bond dissociates on Fe films in a narrow temperature range around 80 K [11]. The narrow temperature range of bond breaking is especially well documented for the sequential decomposition of organic molecules on transition metal surfaces [12]. Temperature programmed desorption studies of alkene decomposition indicates hydrogen evolution in narrow temperature ranges as a result of C–H bond scission [13]. These occur sequentially at well defined temperatures for a given surface. Again, the more open the surface, the lower the temperature of bond dissociation.

All these results, the influence of low coordination number surface atoms on the sequential bond breaking in adsorbed molecules as the temperature is increased and the narrow temperature range of bond dissociation, can be caused by surface atom restructuring. The concerted reconstruction of surface atoms can lead to the narrow temperature range of bond breaking and these effects may occur sequentially, each associated with a different surface restructuring process. Lower coordination number surface atoms are more active for chemical bond breaking because they can restructure more readily.

Recently, it has been shown that small molecules such as CO or CH_4 which impinge on surfaces with higher kinetic energies have also higher dissociation probability [14]. It is also likely that the higher kinetic energy transferred to surface atom vibrations will induce surface restructuring which, in turn, facilitates the bond breaking in the incident molecules.

Catalytic reactions that occur on solid surfaces can be separated into two classes: Those that are surface structure sensitive, and those that are not [15]. The synthesis of ammonia is an example of structure sensitive reactions, as the iron (111) and (211) crystal faces produce ammonia at rates that are over two orders of magnitude greater than the close packed (110) crystal face [7c]. Our mechanism would propose that the adsorption of dinitrogen produces a local surface restructuring that creates the active sites for dinitrogen dissociation to nitrogen atoms, which determines the reaction rate. This restructuring occurs more readily at the more open surfaces of iron. Since the surface geometries that have seven coordinated iron atoms in the second layer under the surface appear to be most active for ammonia synthesis (they are only present in the Fe(111) and Fe(211) surfaces), these local site structures would appear to restructure most readily in a way necessary for dinitrogen dissociation. Thus, there is a good correlation between the structure of the clean surface and the surface structure that exists under steady state reaction conditions in the case of structure sensitive catalytic reactions.

Such a relationship does not seem to exist for structure insensitive reactions. For example, the rate of ethylene hydrogenation to ethane on platinum or rhodium is surface structure independent over a wide temperature range [16]. This has been difficult to understand, as catalytic reactions involve the formation and breaking of chemical bonds with the solid surface and reactions among species bound to the surface. All our surface science studies indicate that the nature of the surface chemical bonds is sensitive to the local surface structures. However, there could exist surface restructuring processes that depend on the adsorbate-adsorbate interaction in addition to the direct interaction between adsorbate and substrate. Especially at high coverages of adsorbates, when the metal surface is almost completely covered, the local chemical bond, as measured by the heat of adsorption, is weakening rapidly with increasing coverage. Since surface restructuring is associated with the formation of chemical bonds with adsorbates, the adsorbate-adsorbate interaction can control the surface restructuring process in this circumstance. Our mechanism of surface restructuring could provide an explanation for the absence of surface structure sensitivity if we assume that for these reactions local surface restructuring is induced by adsorbate-adsorbate interactions. Under identical experimental conditions of pressure and temperature, the same concentration of active sites with the same structure would form by surface restructuring regardless of the clean substrate surface structure. If changes in adsorbate-adsorbate interaction cannot induce surface restructuring, our model cannot be applied to structure insensitive catalytic reactions.

In order to provide experimental verification of the surface restructuring model of bond dissociation and catalytic reactions, the local atomic surface structure must be probed during chemisorption and under steady state reaction conditions along with monitoring changes in adsorbate bonding. The scanning tunneling microscope (STM) or the atomic force microscope (AFM) could provide such information. Non-linear optical techniques such as second harmonic generation (SHG) proved to be sensitive to changes of density of electron states at metal surfaces that would also accompany the surface restructuring process. These techniques can be used at the high pressures necessary to probe the surface structures during chemisorption or catalytic reactions.

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References

[1] J.M. McLaren, J.B. Pendry, P.J. Rous, D.K. Saldin, G.A. Somorjai, M.A. Van Hove and D.D. Vvendensky, in: *Surface Crystallographic Information Service: A Handbook of Surface Structures* (D. Reidel, Dordrecht, Holland, 1987).
[2] F. Jona and P.M. Marcus, in: *The Structure of Surfaces II*, eds. J.F. van der Veen and M.A. Van Hove (Springer-Verlag, Heidelberg, 1988).
[3] M.A. Van Hove, R.J. Koestner, P.C. Stair, J.P. Biberian, L.L. Kesmodel, I. Bartos and G.A. Somorjai, Surf. Sci. 103 (1981) 189.
[4] a. H.D. Shih, F. Jona, D.W. Jepsen and P.M. Marcus, Phys. Rev. Lett. 46 (1981) 731.
b. J.H. Onuferko, D.P. Woodruff and B.W. Holland, Surf. Sci. 87 (1979) 357.
c. L. Wenzel, D. Arvanitis, W. Daum, H.H. Rotermund, J. Stohr, K. Baberschke and H. Ibach, Phys. Rev. B36 (1987) 7689.
d. C.C. Bahr, J.J. Barton, Z. Hussain, S.W. Robey, J.G. Tobin and D.A. Shirley, Phys. Rev. B35 (1987) 3773.
e. P.J. Estrup, J. Vac. Sci. Technol. 16 (1979) 635.
f. W. Puchta, W. Nichtl, W. Oed, N. Bickel, K. Heinz and K. Mueller, to be published.
g. W. Oed, B. Doetsch, L. Hammer, K. Heinz and K. Mueller, to be published.
h. B.J. Hinch, M.S. Foster, G. Jennings and R.F. Willis, Vacuum 33 (1983) 864;
A.H. Smith, R.A. Barker and P.J. Estrup, Surf. Sci. 136 (1984) 327.
i. K. Griffiths, D.A. King, G.C. Aers and J.B. Pendry, J. Phys. C15 (1982) 4921.
j. P.J. Rous, J.B. Pendry, D.K. Saldin, K. Heinz, K. Muller and N. Bickel, Phys. Rev. Lett. 57 (1986) 295.
[5] B.E. Bent and G.A. Somorjai, J. of Advances in Colloid and Interface Science (1988) to be published.
[6] a. J. Sokolov, F. Jona and P.M. Marcus, Europhysics Lett. 1 (1986) 401.
b. G. Kleinle, V. Penka, R.J. Behm, G. Ertl and W. Moritz, Phys. Rev. Lett. 58 (1987) 148.
c. R.J. Behm, G. Ertl and J. Wintterlin, Ber. Bunsenges. Phys. Chem. 90 (1986) 294.

d. R.J. Behm, D.K. Flynn, K.D. Jamison, G. Ertl and P.A. Thiel, Phys. Rev. B36 (1987) 9267.
e. M. Copel, W.R. Graham, T. Gustafsson and S. Yalisove, Sol. St. Commun. 54 (1985) 695.
f. J.A. Yarmoff, D.M. Cyr, J.H. Huang, S. Kim and R.S. Williams, Phys. Rev. B33 (1986) 3856;
U. Doebler, K. Baberschki, D.D. Vvedensky and J.B. Pendry, Surf. Sci. 178 (1986) 679.
g. H. Niehus, C. Hiller and G. Comsa, Surf. Sci. 173 (1986) L599.
h. C.J. Barnes, M.Q. Ding, M. Lindross, R.D. Diehl and D.A. King, Surf. Sci. 162 (1985) 59.
i. B.E. Hayden, K.C. Prince, P.J. Davie, G. Paolucci and A.M. Bradshaw, Sol. St. Commun. 48 (1983) 325.
[7] a. C. Zhang, M.A. Van Hove and G.A. Somorjai, Surf. Sci. 149 (1985) 326.
b. H. Kuroda, T. Ohta, N. Kosugi and Y. Kitajima, in: *Proc. 6th Int'l Conf. Surf. and Coll. Sco.*, Hakone (Japan) June 1988.
c. D.R. Strongin, J. Carrazza, S.R. Bare and G.A. Somorjai, J. Catal. 103 (1987) 213.
d. G.H. Vurens, D.R. Strongin, M. Salmeron and G.A. Somorjai, Surf. Sci. 199 (1988) L387.
[8] M. Simonetta, Nouveau Journal de Chimie 10 (1986) 335.
[9] G.A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell Univ. Press, 1981).
[10] B.E. Bent, G.A. Somorjai and M.A. Van Hove, J. Phys. Chem. 92 (1988) 973.
[11] D.W. Johnson and M.W. Roberts, Surf. Sci. 87 (1979) L255.
[12] M. Salmeron and G.A. Somorjai, J. Phys. Chem. 86 (1982) 351.
[13] B. Bent, C.M. Mate, J.E. Crowell, B.E. Koel and G.A. Somorjai, J. of Phys. Chem. 91 (1987) 1493.
[14] M.B. Lee, Q.Y. Yang and S.T. Ceyer, J. Chem. Phys. 87 (1987) 2724.
[15] F. Zaera, A. Gellman and G.A. Somorjai, Acc. Chem. Res. 19 (1986) 24;
G.A. Somorjai, in: *Catalyst Design, Progress and Perspectives* (John Wiley & Sons, NY, 1987) Ch. 2.
[16] A. Wieckowski, S. Rosasco, G. Salaita, A. Hubbard, B. Bent, F. Zaera and G.A. Somorjai, J. Am. Chem. Soc. 107 (1985) 5910–20;
F. Zaera and G.A. Somorjai, J. Am. Chem. Soc. 106 (8) (1984) 228.