Correlation between catalytic activity and bonding and coordination number of atoms and molecules on transition metal surfaces: Theory and experimental evidence

(catalysis/transition metals/surface structure/electronic structure)

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ABSTRACT   Correlation between catalytic activity and low-energy local electronic fluctuations in transition metals is proposed. A theory and calculations are presented which indicate that maximum electronic fluctuations take place at high-coordination metal sites. Either (i) atomically rough surfaces that expose to the reactant molecules atoms with large numbers of nonmagnetic or weakly magnetic neighbors in the first or second layer at the surface or (ii) stepped and kinked surfaces are the most active in carrying out structure-sensitive catalytic reactions. The synthesis of ammonia from N_2 and H_2 over iron and rhenium surfaces, $^1H_2/^2H_2$ exchange over stepped platinum crystal surfaces at low pressures, and the hydrogenolysis (C—C bond breaking) of isobutane at kinked platinum crystal surfaces are presented as experimental evidence in support of the theory.

Metal catalysts are used to carry out a multitude of selective chemical reactions that range from the synthesis of ammonia from nitrogen and hydrogen gases, to hydrogen–deuterium exchange, to selective hydrocarbon conversion reactions (dehydrocyclization, isomerization, dehydrogenation, and hydrogenolysis to mention a few). These catalysts perform selective bond breaking and rearrangements for millions of turnovers and produce product molecules continuously without deactivation (poisoning). Yet modern surface science studies have revealed by isotope labeling and other appropriate experiments that most of the surface is covered with strongly adsorbed species whose turnover is much longer than the times required to produce the desired products for the catalytic reaction (1). It is therefore obvious that those reaction steps that need metal sites must occur at those few locations on the metal surface that remain uncovered. Thus, the questions arise: How does catalysis occur in the presence of these strongly chemisorbed stagnant layers of almost monolayer coverage? What is the nature of the active metal sites that remain uncovered?

Surface science experiments have also shown that the chemical bonding of adsorbed atoms and molecules is structure sensitive. The heats of adsorption of atoms and molecules could vary as much as 10–30% from adsorption site to adsorption site on the same crystal surface (2). Top, bridge, threefold, and fourfold sites are available on flat, low Miller index surfaces. Surfaces that are rough on the atomic scale are often found, by chemisorption or by catalytic reaction studies, to bind atoms and molecules more strongly and to dissociate strong chemical bonds (N≡N, C—H, C—C, C=O) more readily (2). Rough surfaces are those with higher Miller index, in which the outermost layer is more sparsely populated, thereby exposing atoms in the second and other inner layers [for example the (111) face of a

body-centered cubic (bcc) crystal as opposed to the (110) face, or the (11$\bar{2}$0) surface of a hexagonal-close-packed (hcp) crystal as opposed to the closed packed (0001) face], or have a high concentration of step edges and kink vertices. The structures of some of these surfaces are shown schematically in Figs. 1–5.

One of the key questions in heterogeneous catalysis that emerges from modern surface science studies concerns the determination of those metal sites where catalytic processes occur (3–6); these must be distinctly different from the sites where strong bonding of atoms and molecules takes place accompanied by a low reactivity and slow turnover. In this paper a theory is presented that argues that catalysis is predominant at high-coordination sites: the more bulk-like the site, the greater the probability of electron-state fluctuations, which participate catalytically in the breaking and formation of chemical bonds and yield high turnover. This model points out the catalytic importance of metal atoms located in the second layer of open surface structures—the iron (111) surface for example—which are highly coordinated but are nonetheless exposed to the incoming reactant molecules. Similarly, the increased activity at stepped surfaces is explained by the exposure of high-coordination atomic sites at the bottom of the steps.

Adsorbates tend to form strong stable bonds at lower-coordination sites, where the atoms have few electron-state fluctuations, where s- and p-bonding predominates, and where charge-transfer processes are more common; all these effects lead to the formation of more stable surface compounds. These low-coordination sites have only secondary
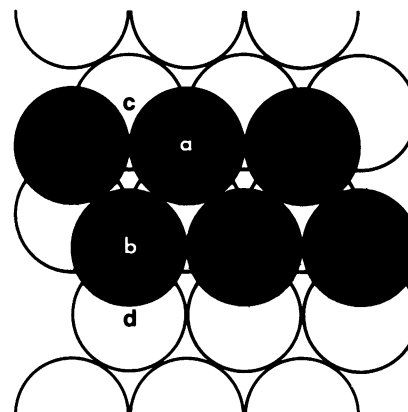

FIG. 1. Geometry for a stepped (111) surface in the face-centered-cubic (fcc) structure. Open circles represent atoms in the second layer, which is complete. Solid circles represent atoms in the first layer, in which every third row is removed to create steps. This arrangement can also describe a stepped (0001) surface of a hcp structure (the difference between the two appears in the third, unseen, layer).
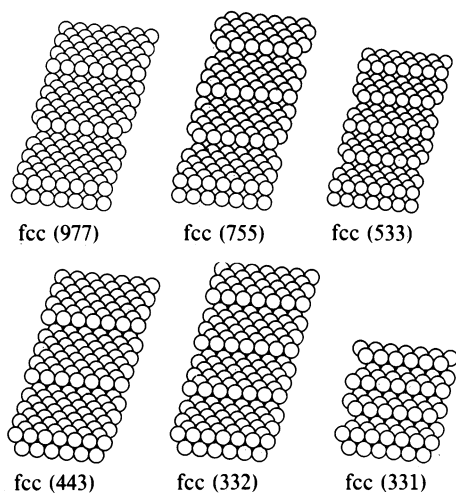
FIG. 2. Various stepped surfaces in the close-packed fcc lattice.

importance in catalytic reactions that require specific metal sites, as they may sterically block catalytically active high-coordination atomic sites, participate in diffusion or atom transfer processes, or change the local work function.

THEORY

The chemisorption of an atom or molecule B at a given location in an A transition-metal surface is essentially a consequence of the local electronic properties both of the atom or molecule and of the metal site or sites in the immediate neighborhood.

A given electronic configuration of, say, an isolated transition-metal atom A and atom B either leads to the formation of a stable AB compound or yields an unreactive no-compound-formation situation. This typical either-or reaction situation is the opposite to what is needed in an effective catalyst, where in principle A should attract B to form a weakly bound AB intermediate compound but be readily available to release B in the presence of C so that the final product BC be formed and A be ready to start the process all over again.

This traditional view of the intermediate-compound theory of catalysis can be viewed from a different point of view: *the particular transition-metal atom A under consideration should be susceptible to stable low-energy electronic fluctuations in its original state.* In that case the intermediate AB compound—intrinsically related to the fluctuations—can be easily formed. Since low-energy fluctuations are also present after a *weak* AB is formed, the compound can also be easily broken and the catalytic reaction may thus take place. The electronic fluctuations of importance may be of many kinds. In particular:

(*i*) Charge fluctuations, in which the electronic charge in the vicinity of A fluctuates about its mean value. Atoms of a metal are the traditional examples of charge fluctuators. The classical noninteracting band model of alkali metals consists of a bulk atom neutral on the average, but with a 1/4 probability each of being positively or negatively singly charged. Electron–electron coulomb repulsion tends to decrease or suppress large charge fluctuations.

(*ii*) Configuration fluctuations, in which the occupation numbers of single-electron orbitals are no longer good quantum numbers. Transition-metal and rare-earth compounds and structures are typical examples of configuration fluctuators. The nickel configuration alternates, for instance, between $(3d)^{10}$, $(3d)^9(4s)^1$, and $(3d)^8(4s)^2$. The cerium atom, a commonly known valence or configuration fluctuator, has its
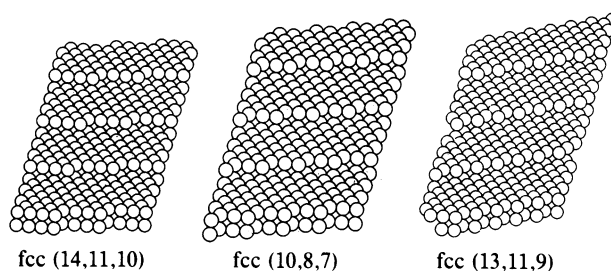

FIG. 3. Various kinked surfaces in the close-packed fcc lattice.

four outer electrons fluctuating among the $4f$, $5d$, and $6s$ shells.

(*iii*) Spin fluctuations, in which the magnitude and the orientation of the local magnetic moment fluctuates about its mean vectorial value. Spin fluctuations are common in the rare-early and in the $3d$-transition-metal compounds.

(*iv*) Term and multiplet fluctuations, present in incomplete shells of complex structure, and common in transition-metal, rare-earth, and actinide elemental and compound solids.

All these fluctuations require the presence of low-energy electronic excitations which must have a large spectral weight in the catalytically active site.

The most important criterion in determining the presence or absence of fluctuations is the location of a given element in the periodic table. There are several tabulations of the heat of adsorption of small molecules (CO, H_2, O_2, N_2) on transition metals that exhibit decreasing values with increasing d-shell occupancy (7). There are also correlations reported for the variations of catalytic activities for hydrogenolysis, hydrogenation, and other chemical reactions that show trends dependent on d-shell occupancy (8, 9). From this evidence it is clear that *the catalytic activity of the transition-metal atoms and ions is directly related to their unfilled d shells.*

Both s and p shells tend to form deep-lying filled (bonding) orbitals, highly energetic unoccupied antibonding orbitals, or wide metallic conduction bands with a relatively low density of states at the Fermi level. None of these situations leads to the sought-for low-energy fluctuations.

The highly degenerate f shells are dominated by the very strong electron-electron intrasite coulomb repulsion. Therefore f levels are essentially atomic in character: most local charge and configuration fluctuations are suppressed. The levels are discrete and only occasional configuration or term fluctuations, as is the case of cerium, survive.

The d shells provide the ideal happy medium: the 10-fold degeneracy and relative narrowness of the bands provide metallic character with a high density of states. But the bands are not dominated by coulomb repulsion effects with the consequent "discretization" of the spectrum, appearance of energy gaps, formation of magnetic moments, and loss of "metallic" character of the d orbitals—all conditions that lead to the suppression of local electronic fluctuations.

The effect changes across the periodic table. The electronic fluctuations increase in going from the $3d$ to the $4d$ to the $5d$ series: the d bandwidth increases in that direction, the coulomb repulsion effects are less dominant, magnetism disappears, and ordinary configuration fluctuations increase. The effect increases from left to right in the periodic table: the group VIII elements are the most favorable.

Because of computational considerations we have explored theoretically in detail the local electronic structure of various surfaces of the late $3d$ transition metals: Ni, Co, Fe, and Cr. We have also explored heterogenous structures involving either two of these elements or one of the elements and their noble-metal neighbor, Cu.

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Table 1. Number n of d holes for nickel atoms in various configurations

Configuration	$Z(Ni)$	$Z(Cu)$	n
Bulk nickel	12		0.56
(111) Surface nickel atom	9		0.38
Outstep nickel atom a (Fig. 1)	7		0.25
Outstep nickel atom b (Fig. 1)	7		0.24
Instep nickel atom c (Fig. 1)	11		0.52
Instep nickel atom d (Fig. 1)	10		0.45
Ni under a (111) Cu monolayer	9	3	0.52
Ni monolayer on Cu (111)	3	6	0.46

Nickel is particularly interesting, since it is the last of the $3d$ group VIII transition metals. When nickel is in its metallic form, the ground state is a mixture of three configurations (10) that, on the average, result in the d shell being occupied by 9.44 electrons. The presence of the $n = 0.56$ d holes, which are a measure of the configuration fluctuations, is responsible for the catalytic activity of Ni. The larger n, the larger the configuration fluctuations of a particular Ni atom, and the greater the catalytic activity of that particular site. Our calculations for nickel in its paramagnetic state—which should also be applicable to palladium and to platinum—yield a close correlation between n and the coordination number Z of a particular site (10). Our results are shown in Table 1, where $Z(A)$ denotes the number of nearest neighbors of chemical species A.

An analysis of these results yields the following simple conclusion: *configuration fluctuations are larger for those atoms that have a large number of metallic neighbors.* Therefore transition-metal atoms in sites that are bulk-like, have a high metallic coordination, and are accessible to the reactants should be, according to this argument, catalytically active.

Another measure of the fluctuations in transition metals is the local spin imbalance at each site. When the coulomb repulsion between electrons becomes strong enough, the system tends to lessen or minimize its influence by suppressing metallic fluctuations. This suppression results in a tendency either towards an insulating state or to the formation of magnetic states (11, 12) with local spin imbalance (local magnetic moment) and, at low temperatures, long-range magnetic order (ferromagnetic, antiferromagnetic, ferrimagnetic, spiral arrangements, etc.). Those conditions that lead to the formation or enhancement of spin imbalances do not favor—i.e., they suppress or decrease—catalytic activity.

We have calculated the spin imbalance S (twice the local magnetic moment divided by the g-factor) for a variety of structures, sites, and circumstances (13–19). Our results are shown in Table 2.

Since spin imbalances are one of the manifestations of reduced fluctuations, we expect, for a given element, catalytic activity to be anticorrelated to its spin imbalance. This anticorrelation and our calculations (Table 2) point once again to catalytically active sites in locations of high coordination, and preferentially to *atoms surrounded by a large number of nonmagnetic or weakly magnetic metallic neighbors.*

EXPERIMENTAL EVIDENCE

We present here experimental evidence for the high catalytic activity of atomically rough surfaces, where high-coordination sites in the first or second layer at the surface are exposed. We also show how stepped surfaces that expose

Table 2. Spin imbalance S of the magnetic transition metals in various configurations

| Configuration	$Z(Ni)$	$Z(Cu)$	$Z(Fe)$	$Z(Co)$	$Z(Cr)$	S
Ferromagnetic bulk fcc nickel	12					0.56
Nickel in Ni$_3$Cu quenched alloy	8	4				0.42
Nickel in NiCu quenched alloy	4	8				0.08
Nickel in NiCu$_3$ quenched alloy	0	12				0
Nickel at the (100) free surface	8					0.74
Nickel at the (111) free surface	9					0.65
Nickel under a (100) Cu monolayer	8	4				0.37
Nickel under a (111) Cu monolayer	9	3				0.38
Nickel monolayer on top of Cu (100)	4	4				0.48
Nickel monolayer on top of Cu (111)	6	3				0.08
Ferromagnetic bulk hcp cobalt				12		1.56
Cobalt in the FeCo ordered alloy			8	0		1.78
Cobalt at the (100) surface of the FeCo alloy			4	0		2.03
Cobalt at the (110) surface of the FeCo alloy			6	0		1.86
Cobalt monolayer on top of Cu (111)		3		6		1.63
Ferromagnetic bulk bcc iron			8			2.12
Iron in the FeCo ordered alloy			0	8		2.66
Iron at the (100) free surface			4			2.90
Iron at the (110) free surface			6			2.55
Iron at the (100) free surface of the FeCo alloy			0	4		2.95
Iron at the (110) free surface of the FeCo alloy			0	6		2.75
Iron under a (100) Cr monolayer			4		4	1.95
Antiferromagnetic bulk chromium (incommensurable phase)					8	0.59
Antiferromagnetic bulk chromium (commensurable phase)					8	0.67
Chromium at the (100) free surface					4	3.00
Chromium at the (110) free surface					6	2.31
Chromium monolayer on top of Fe (100)			4		0	3.63
Chromium monolayer on top of Fe (110)			2		4	2.25
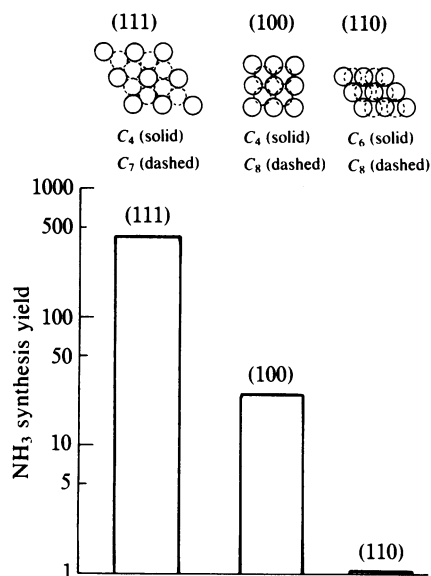
FIG. 4. Surface structure sensitivity of iron-catalyzed ammonia synthesis. The symbols C_n indicate n-coordinated sites. Yield is expressed in arbitrary units.
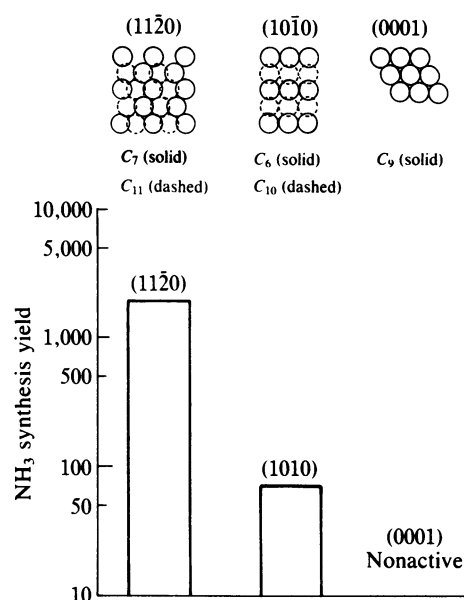

FIG. 5. Strong surface structure sensitivity of ammonia synthesis on rhenium single crystals. Symbols as in Fig. 4.

high-coordination sites at the step inner edges and at kinks exhibit high turnover rates for various reactions.

Greatly Enhanced Rates of Ammonia Synthesis on Open Crystal Faces of Iron and Rhenium That Expose the High-Coordination Atoms in the First and Second Layers. The rate-determining step in the synthesis of NH_3 from N_2 and H_2 is the dissociation of N_2 (20). Chemisorption studies indicate that on the open (111) crystal face, where the high-coordination iron atoms in the second layer are exposed to the incoming nitrogen molecules, the dissociation probability of N_2 is much higher than on the close-packed (110) face. Chemical reaction studies on iron single crystal surfaces, shown in Fig. 4, revealed that the rate of ammonia formation is 500 times greater on the Fe (111) than the Fe (110) face, while the Fe (100) face exhibits catalytic activity that is intermediate between the other two crystal faces (3).

The closed-packed hexagonal (0001) face of rhenium is virtually inactive for the synthesis of ammonia, while the open (10$\bar{1}$0) and (11$\bar{2}$0) crystal faces have high reactivities, many orders of magnitude higher than the (0001) face (4). These active crystal surfaces exhibit an open structure with many high-coordination sites exposed to the incoming molecules both in the first and in the second layers at the surface. In Fig. 5 we show the relative reaction rates on the different single crystal surfaces along with the surface structure, displaying atoms of different nearest-neighbor configurations.

Reactive Molecular Beam Surface Scattering Studies of $^1H_2/^2H_2$ Exchange on Stepped Platinum Single Crystal Surfaces. The reaction of hydrogen and deuterium molecules to form $^1H^2H$ is one of the simplest reactions that take place readily on transition-metal surfaces, even at temperatures as low as 100 K. This reaction was studied by using mixed molecular beams of $^1H_2$ and $^2H_2$ on the (111) and stepped surfaces of platinum (5). The reaction probability was 0.35 on the stepped surfaces, much higher than the 0.07 value on the (111) surface under identical experimental conditions. The reaction probability also depended markedly on the direction of approach of the reactant molecules to the stepped surface. This is shown in Fig. 6. The production of $^1H^2H$ was the highest when the reactants struck the open side of the step structure, and it decreased by about a factor of 2 when the inner edge of the step was shadowed. These results indicate that the inner corner atom, which is also the one with the

highest coordination, is the most active for breaking the large binding energy (103 kcal/mol) of the H—H bond.

Enhanced Hydrogenolysis Activity at Kink Sites on Platinum Crystal Surfaces. Platinum is widely used as a catalyst for the rearrangement of hydrocarbons. It is particularly useful for the conversion of straight chain alkanes to aromatic molecules and branched isomers, to produce gasoline with high octane number. The conversion of n-hexane or n-heptane is often used as a test reaction that probes the selectivity of various platinum crystal surfaces to yield the

Angle of incidence (θ), degrees
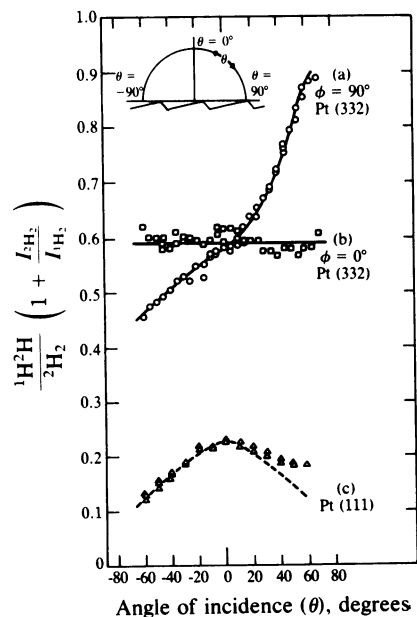
FIG. 6. Reaction probability for $^1H_2/^2H_2$ exchange over a platinum single crystal surface as a function of angle of incidence θ of the molecular beam, normalized to the incident $^2H_2$ intensity. Curve a, the platinum (332) surface with the step edges perpendicular to the incident beam. Curve b, the platinum (332) surface where the projection of the beam on the surface is parallel to the step edges. Curve c, the smooth, close-packed platinum (111) surface. ϕ, Angle of azimuth; I, beam intensity. Frequency of chopping was 10 Hz and surface temperature was 800°C.