Electronic nature how size dominates the surface reactivity of nanomaterials

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Abstract:
Size reduction can generally increase and dominate the surface reactivity of nanomaterials, and leads to size-dependent catalysis, but the underlying physical and chemical principles have not been revealed by experiments or computer simulations. In this paper, the general electronic nature dominating surface reactivity is revealed through establishing physical and mathematical models describing the electronic processes of chemisorption. The central point is that chemisorption can competitively redistribute surface valence atomic orbitals from energy bands to surface coordination bonds. A general mathematical criterion is derived to judge the structure effects on surface reactivity based on a concept of orbital potential. Further, the electronic nature of why and how size can dominate the surface reactivity of nanomaterials is mathematically explained, which lies in the dominating contribution of size (the number lattice atoms) to the orbital potential of the whole particle applied to surface atoms.

Nanomaterials can display size-dependent surface reactivity when their sizes are below certain critical values. This widely leads to enhanced performances of heterogeneous catalysis, electrocatalysis, surface ligation, etc. In particular, the most representative phenomenon is the emerged catalytic capability of gold nanoparticles smaller than 5.0 nm. Vast efforts have been made to understand the origin mechanisms of such size-dependent surface reactivity, however, the issue still cannot be clearly answered by a general model or theory. Basically, it is highly challenging to reveal the electronic nature of why and how size reduction can increase and dominate surface reactivity merely through experiments or computer calculations. This is because surface reactivity is affected by all structure parameters, including electronic, atomic, geometrical and interfacial factors. The complexity increases the difficulties to control variables when studying a specific structure effect. In particular, it is worth noting that size, shape and surface area are just geometrical parameters, rather than the in-depth physical nature. Some reports attributed the origin of enhanced catalytic reactivity of Au nanoparticles to the increased ratios of surface defect sites, which neglected the roles of decreased size. Theoretically, the evolution trends of surface reactivity should be ruled by a general physical principle, which can cover the effects of all structural factors despite the forms of adsorbates and surfaces.

Establishment of such an insightful principle relies on developing reasonable physical and mathematical models that catch the general electronic nature of adsorbate-surface
interaction through chemisorption\textsuperscript{25,26}. In this paper, we devoted to developing a general principle to understand the electronic nature of why and how size reduction increases and dominates the surface reactivity of nanomaterials. This was realized based on analyzing the electronic feature of chemisorption of competitive orbital redistribution. A mathematic model was deduced as a general criterion to judge the evolution trends of structure effects on surface reactivity. The roles of particle size were explored with the model, and we gave the general electronic nature of why and how size dominates surface reactivity. In this theory, the orbital potential that measures the bonding ability of surface atoms is a critical parameter.

**Figure 1. Physical model of chemisorption based on competitive orbital redistribution.** (a) Scheme shows the orbital redistribution induced by an adsorbate. The valence atomic orbitals of surface atoms tend to distribute into the bulk lattice to contribute to energy bands. Surface adsorbate can polarize part of the atomic orbital of an active site from band states to form a surface coordination bond. (b) Electronic diagram of a surface chemical bond. This case illustrates the interaction between adsorbate’s HOMO and an unoccupied atomic orbital of a surface atom. The HOMO overlaps with the surface orbital and shares certain electron pairs (\(\delta\)) to form a surface coordination bond.

Chemisorption deals with the chemical interactions of adsorbates on solid surfaces, in which the critical feature is the formation of surface coordination bonds\textsuperscript{25}. As illustrated in Fig. 1a, the interactions occur through overlapping the frontier molecular orbitals (MOs) of adsorbates and the valence atomic orbitals of surface atoms, and further repopulating the valence electron pairs. The results of chemisorption are to redistribute the orbitals, weaken or break old bonds, and change the electronic structures of both adsorbates and surfaces. This electronic process is the physical origin of chemisorption to activate molecules, in which the surface reactivity positively correlates to the strength of chemisorption.
The electronic features of solids are their energy bands, which result from the extended overlaps of their valence atomic orbitals (VAOs) and delocalized populations of valence electrons. Different from the bulk atoms, the VAOs of surface atoms (SVAOs) mainly distribute in two forms as shown in Fig. 1a, delocalized into the lattice to form energy band states and localized into surface chemisorption bonds. Without adsorbates, SVAOs tend to delocalize into energy bands. While adsorbates can perturb the surface electronic states through polarizing SVAOs of active sites from energy band states to localized chemisorption bonds as shown in Fig. 1b. The frontier molecular orbitals of adsorbates, highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO), interact with the energy bands of solids, which is realized through forming localized chemisorption bonds. As illustrated in Fig. 1b, the HOMO of adsorbate overlaps with a specific SVAO and shares its electron pair to form the surface bond. As a result, part of the SVAO is extracted from the band states and confined into surface state. Such a redistribution process of SVAOs can be described with distribution fraction ($f$) of an atomic orbital, which is the square of electronic wavefunction.

We use $f_B$ to denote the contribution of a SVAO to energy bands, and $f_S$ to represent its fraction into chemisorption bond. For fixed material and adsorbate, $f_S$ can serve as a descriptor measuring the strength of chemisorption, that is increased $f_S$ indicates enhanced chemisorption. According to the quantum normalization postulation of electronic wavefunctions, we can always have

$$f_S + f_B = 1 \quad (1).$$

The values of $f_S$ and $f_B$ belong to [0, 1], thus eq. (1) indicates that $f_S$ and $f_B$ are competitive. We can further conclude that the electronic nature of increasing surface reactivity is to competitively increase $f_S$ but simultaneously decrease $f_B$.

At a stable chemisorption state, we can have a fixed $f_S/f_B$ ratio. The ratio is ultimately determined by the powers of adsorbates and solid phases to form and stabilize chemical bonds with the same SVAO. This power is an intrinsic electronic property of adsorbates and solid surfaces, and completely determines surface reactivity. Here we introduce a concept, orbital potential ($G$), to describe this competition power. Basically, $G$ is a function of all structural parameters, including composition, long-range and local atomic structures, facet, particle size, adsorbate, coverage, defect, strain, coordination number, etc. For an equilibrium chemisorption state, we have

$$\frac{f_S}{G_S} = \frac{f_B}{G_B} \quad (2),$$

where $G_S$ is the orbital potential of an adsorbate, and denotes the bonding capability of the adsorbate to a SVAO; $G_B$ is the orbital potential at a surface site applied by the whole solid phase. Solving eq. (1) and (2), we obtain,

$$f_S = \frac{G_S}{G_S + G_B} = \frac{1}{1 + \frac{G_B}{G_S}} \quad (3)$$

and

$$f_B = \frac{G_B}{G_S + G_B} \quad (4).$$

Eq. (3) suggests that chemisorption strength can be enhanced by decreasing the ratio of $G_B/G_S$, that is to increase $G_S$ and decrease $G_B$. In general, $G_S$ is the driving force while $G_B$ is the resistance for increasing surface reactivity. As $G$ is the function of all structural parameters, and surface reactivity is practically tuned by varying structural parameters, the surface reactivity can be further expressed as
\[ f_S = f_S(\vec{x}) \] (5),

where \( \vec{x} \) represents all structural factors. Then \( f_S \) can be expanded as

\[ f_S = f_{S0} + \Delta f_S = f_{S0} + \sum \int \frac{\partial f_S}{\partial x_i} dx_i \] (6),

where \( f_{S0} \) denotes the intrinsic surface reactivity on macroscale single crystals. \( \dot{f}_S = \frac{\partial f_S}{\partial x_i} \) denotes the effect of structural parameters on surface reactivity, which actually is the structure-function relationship of surface reactivity. As \( f_S \) is the function of \( G_S \) and \( G_B \), eq. (6) can be rearranged as

\[ f_S = f_{S0} + \sum \int \left( \frac{\partial f_S}{\partial G_S} \cdot \frac{\partial G_S}{\partial x_i} + \frac{\partial f_S}{\partial G_B} \cdot \frac{\partial G_B}{\partial x_i} \right) dx_i \] (7).

With eq. (3), eq. (7) can be written as

\[ f_S = f_{S0} + \sum \int f_S f_B \left( \frac{\partial G_S}{\partial G_S} - \frac{\partial G_B}{\partial G_B} \right) dx_i \] (8).

The mathematic expression of structure-function relationship of surface reactivity is

\[ \frac{\partial f_S}{\partial x_i} = f_S f_B \left( \frac{\partial G_S}{\partial G_S} - \frac{\partial G_B}{\partial G_B} \right) \] (9).

We define

\[ X = \frac{\dot{G}_S}{\dot{G}_S} - \frac{\dot{G}_B}{\dot{G}_B} \] (10).

As \( 0 \leq f_S f_B \leq 1/4 \), the plus or minus of eq. (9) depends on the sign of \( X \). Then \( X \) is the criterion determining the tendencies of structure factors to tune surface reactivity. We call \( X \) as reactivity evolution indicator. For fixed adsorbates \( \dot{G}_S = 0 \), then

\[ X = -\frac{\dot{G}_B}{\dot{G}_B} \] (11).

Eq. (11) means that the structure effect on surface reactivity totally depends on the sign of \( \dot{G}_B \). Negative \( \dot{G}_B \) yields positive \( X \), then increased surface reactivity results from increased \( x \), like defects; while positive \( \dot{G}_B \) leads to negative \( X \), thus decreasing \( x \) will increase surface reactivity, like size and coordination number. In a word, the general rule to increase \( f_S \) is to decrease \( G_B \).

\[ \text{Figure 2. Spherical model of a particle with a radius of } R. \text{ In this model, point } C \text{ is the surface active site. The binding capacity at point } C \text{ to the surface atomic orbital comes from the effective electrostatic force applied by the whole particle.} \]

For given material and adsorbate, surface reactivity is affected by the structural factors of the substrate, like particle size, exposed facet, defect and coordination number. At the nanoscale, size is the primary factor, which can even dominate the effects of others. But the underlying electronic principle has not been completely understood. According to eq.
the critical point is to find out how size correlates to $G_B$, that is the function of $G_B = G_B(R)$. 

To get a general insight into the electronic nature of size effects on surface reactivity, we use a sphere with a radius of $R$ and uniformly distributed nuclear charges to model a particle. Assuming the effective nuclear charge is $q_0$ for each structure unit with a volume of $V_0$, then the charge density is $q_0/V_0$ within the whole particle. As shown in Fig. 2, the point C with a rectangular coordinate of $(0, 0, R)$ is set as the chemisorption site. We presume the orbital potential at point C comes from the effective electrostatic force applied by the whole particle. Therefore, according to Coulomb's law, the electric field applied to point C by any point A within the particle is

$$dE = \frac{k q_0}{V_0} dV \cdot \frac{r_{CA}}{r_{CA}} \cdot \frac{1}{r_{CA}}$$

(12),

where $r_{CA}$ is the distance from C to A, and $k$ is Coulomb’s constant. Then the effective total electronic field felt by point C can be calculated by integrating eq. (12) over the whole particle,

$$E = \iiint k \frac{q_0}{V_0} \frac{1}{r_{CA}} \cdot \frac{r - r \cos \theta}{r_{CA}} dV$$

(13).

In spherical coordinate eq. (13) can be rewritten as

$$E = \iiint k \frac{q_0}{V_0} \frac{r - r \cos \theta}{r_{CA}^2} \cdot r^2 \sin \theta \,dr\,d\theta\,d\varphi$$

(14).

With $r_{CA} = 2r \sin \frac{\theta}{2}$, eq. (14) can be further simplified as

$$E = \iiint k \frac{q_0}{V_0} \frac{\cos \frac{\theta}{2}}{2} \,dr\,d\theta\,d\varphi$$

(15).

Integrating eq. (15) with $0 \leq r \leq R$, $0 \leq \varphi \leq 2\pi$ and $0 \leq \theta \leq \pi$ results in

$$E = \frac{\pi k q_0}{V_0} R$$

(16).

Thus we have

$$G_B = \frac{\pi k q_0}{V_0} R$$

(17)

and

$$X = -\frac{G_B}{G_B} = -\frac{1}{R}$$

(18).

For the ideal particle, eq. (6) becomes

$$d\bar{f}_S = -f_S(1 - f_S) \frac{dR}{R}$$

(19).

Integrating eq. (19) gives

$$f_S = f_{S_0} + \frac{f_{S_0}}{cR + 1}$$

(20),

where $c$ is a positive constant correlating to the intrinsic surface reactivity $f_{S_0}$. Eq. (20) suggests that surface reactivity inversely correlates to particle size, which explains the origin of size effect on surface reactivity.

As the orbital potential on SVAOs dominantly comes from the bonding ability of the bulk atoms, thus size is the primary factor affecting this force. Compared to size, other structural factors, such as defect, strain and dopant, are minority species. They can only apply limited effects on surface reactivity, and the effect is also dependent upon the distances between these defect sites and surface active sites. Considering the reactivity effects of other structural factors on a spherical particle with a constant size, then eq. (9) becomes,
\[
\frac{\partial f_S}{\partial x_i} = -f_S f_B \frac{\nu_0}{\pi k q_0} \frac{\dot{G}_B}{R} \quad (21),
\]

where \( \dot{G}_B \) denotes the effects of other structural parameters on orbital potential.

Eq. (21) suggests that the effects of all other structural factors on surface reactivity are coupled to size. In general, the effects of other structural factors can be amplified by decreasing particle size. Therefore, eq. (21) reveals the general physical nature of why and how size dominates the surface reactivity of nanomaterials. Such an amplification effect resulting from size reduction is a core feature of the surface science of nanomaterials, which distinguishes nanoscale surface science from macroscale surface science.

In conclusion, the general electronic nature of why and how size reduction can increase and dominate the surface reactivity of nanomaterials is revealed by establishing mathematical models describing the competitive orbital redistribution processes induced by chemisorption. A general mathematical criterion to judge the evolution effects of structural factors on surface reactivity is derived, in which orbital potential \( (G) \), the capability of adsorbate or surface to stabilize surface atomic orbitals, is the critical parameter. Mathematically, we find that surface reactivity is inversely proportional to particle size, and the effects of other structural factors is inversely coupled to particle size. The correlations indicate that size reduction can increase the surface reactivity of nanomaterials, and can also amplify the effects of other structural factors, such as defect, on enhancing surface reactivity. The underlying physical nature is that the orbital potential of solid phase is dominately contributed by the lattice atoms, which positive correlates to the number these lattice atoms, that is particle size.

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