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From Surface of Model Catalyst in UHV to Surface of Nanoparticle Catalyst During Catalysis

Surface has been one of the most important states other than the routine three states or called three phases including solid, liquid, and gas. Surface of a catalyst can be considered as a special solid state since most heterogeneous catalysts are at a solid state. The reason that it can be called a special solid state is its structural imperfection. The imperfection is laid on two aspects including its topmost atomic layer and subsurface. An imagination for producing such a special solid state in terms of a surface is to cut a crystal from the middle. This cutting creates two surfaces. The coordination environment of atoms of the topmost layer (Figure 1.1a) is distinctly different from those of an atomic layer in bulk.

The difference in coordination environment including coordination number and interatomic distance between the topmost atomic layer/subsurface and atomic layers in bulk is the origin of the surface activity or reactivity. The coordination environment of an atom of the topmost atomic layer can be termed undercoordination. The broadly defined undercoordination is the origin of catalytic activity of a heterogeneous catalyst since a catalytic reaction involves bonding to surface of a catalyst and is performed on the surface. The origin of catalytic activity at undercoordination is true even for catalysis on a bent internal surface in a microporous material. Notably, the internal surface of a micropore creates confinement effect that is an additional origin for catalytic activity in a great number of high temperature catalytic reactions of hydrocarbons and low-temperature chemical transformation of methane.[2–4] Origin of catalytic activity of a microscopic aluminosilicate catalyst with bent internal surface is an important topic. Here we focus on catalysis on the open surface of a solid catalyst.

Pt(111) is the simplest model surface (Figure 1.1a). Each Pt atom on the surface coordinates with six Pt atoms in the same atomic layer and three in the next layer. It has three open coordination spots and thus exhibits a tendency to adsorb an atom or a molecule. For instance, C atom of a CO molecule forms a Pt—C bond; this binding is enhanced by a backdonation of *d* electrons of the Pt atom to the antibonding orbital of CO molecule, $2\pi^*$. The formation of a surface bond between a reactant molecule and the topmost atom of a catalyst weakens the intramolecular bond of a CO molecule. The weakening of this C≡O bond can either facilitate dissociation of CO or trigger an attack from an atom, molecule or intermediate such as a binding of a H atom to either C or O atom of the activated CO molecule. Obviously, the surface openness in terms of undercoordination of the surface atoms initiates the surface reactivity or catalytic activity.

Application of Ambient Pressure X-ray Photoelectron Spectroscopy to Catalysis, First Edition. Franklin Tao.

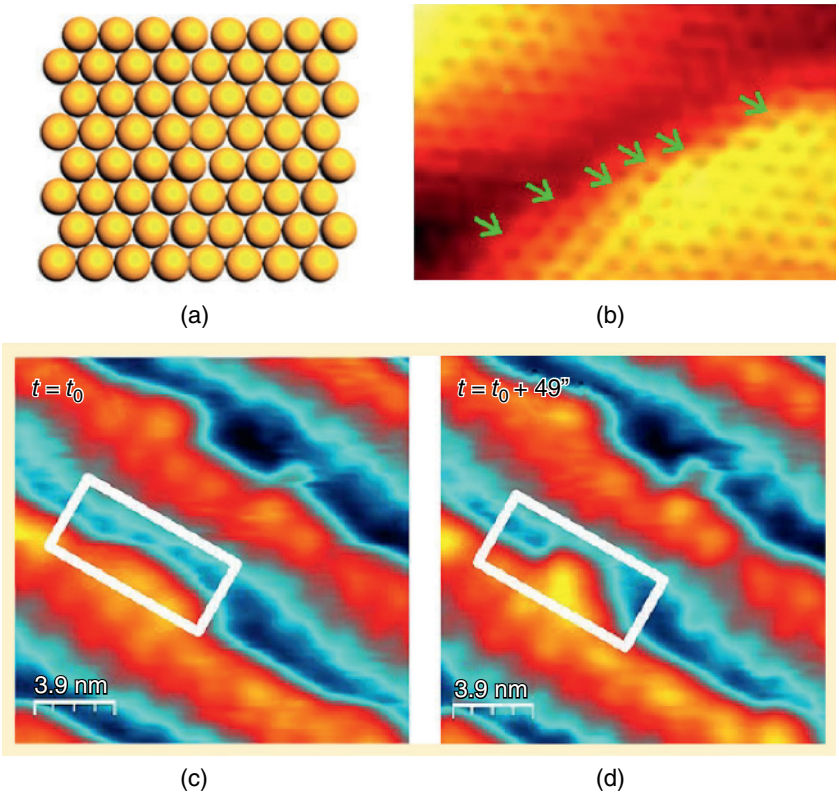

Figure 1.1 Surface structural model and scanning tunneling microscopy (STM) images of a real surface. (a) Pt(111) surface; each Pt atom bonds with six atoms of the topmost layer and three of the next layer (not drawn). (b) STM image of irregular packing of atoms at edge of a terrace on Pt(111) in 1 Torr CO. (c and d) STM images of the same area of Pt(111) single crystal model catalyst in 10 Torr CO collected at $t = t_0$ and $t = t_0 + 49$ seconds, respectively. The two images showing an evolution of the edge of a terrace within 49 seconds through repacking atoms at the edge of a terrace in 0.1 Torr CO at room temperature; the two images were taken at the same location on Pt(111). *Source:* Reproduced with permission from Nguyen et al.[1]/American Chemical Society.

It is not inappropriate to imagine a (111) surface drawn on a paper is perfect and all atoms are coordinated with nine Pt atoms. However, a real surface is way more complicated than the drawn. As shown in Figure 1.1b, even the simplest surface of Pt(111) single crystal could have certain portion of Pt atoms at step edge where a Pt atom coordinates with less than nine Pt atoms. These undercoordinated Pt atoms at step edge can be readily restructured. As seen in Figure 1.1c and d, the Pt—Pt bonds are readily broken at room temperature to form a peninsula-like cluster while a Pt(111) single crystal model catalyst is in a CO gas at a pressure as low as 0.1 Torr.[1] Clearly, we can simply claim the surface of a catalyst is full of defects. These defects make the surface act as an active reagent to participate in a chemical reaction of gaseous or/and liquid reactants, but the solid surface in terms of the catalyst is not consumed.

Pt(557) is relatively more complicated than Pt(111). As shown in Figure 1.2a, a Pt(557) surface has at least three different types of Pt atoms that coordinated with 7, 9, or 10 atoms,

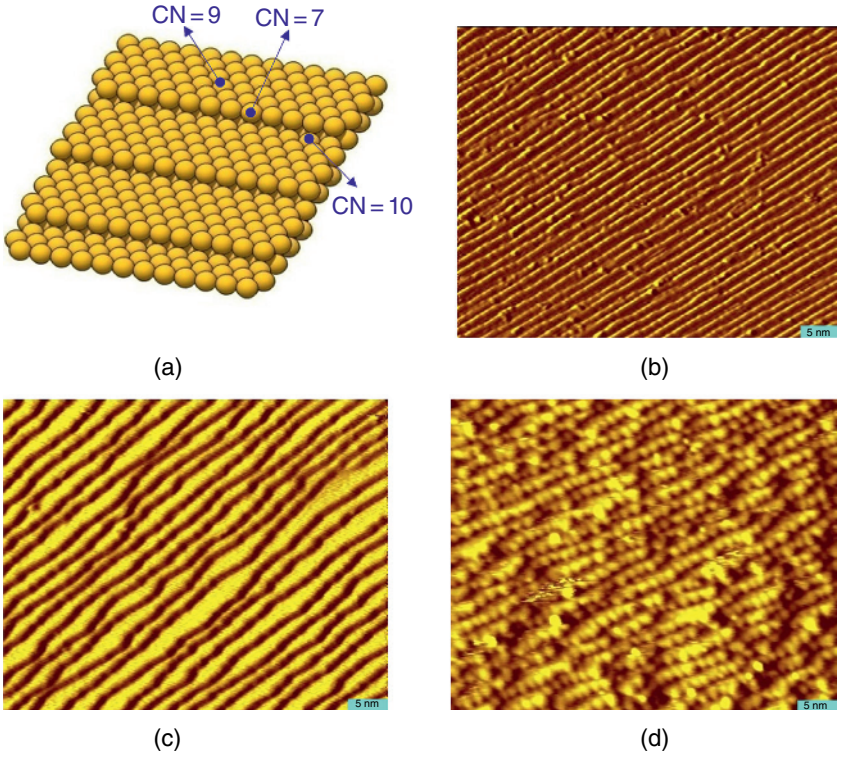

Figure 1.2 Structural model of a stepped model catalyst Pt(557) and evolution of its surface structure along increase of pressure of CO gas surrounding the model catalyst. (a) Structural model of Pt(557). *Source:* Adapted from Tao et al.[5] (b) STM image of clean Pt(557) at room temperature in UHV with a base pressure lower than 3×10^{-10} Torr. (c) STM image of Pt(557) at room temperature in 5×10^{-8} Torr CO. (d) STM image of Pt(557) at room temperature in 1 Torr CO. *Source:* Reproduced with permission from Tao et al.[5], Reprinted from AAAS.

respectively. The atoms within each terrace are just like atoms on Pt(111), coordinating with nine atoms. These atoms at the edge of a terrace or called a step have coordination number of 7. In addition, Pt atoms immediately under the step edge are partially exposed, coordinating with 10 atoms (Figure 1.2a). Notably, if one or two Pt atoms at step edge are removed, a kink site is created (Figure 1.3c). Typically, a Pt atom of a kink site coordinated with six Pt atoms or less. As these step-edge atoms have a low coordination number, 7, the Pt—Pt bonds at the step edge can be readily broken, resulting in a restructuring of the step edge in CO at a pressure as low as 1×10^{-8} Torr CO (Figure 1.2c). As the width of each step is narrow, a continuous break of Pt—Pt bonds and the resulting relocations of more Pt atoms make the step broken down.[1,2] Through forming an intermediate surface phase in terms of a double width terrace, the surface is broken into triangular nanoclusters with a width of 2.2 nm or so (Figure 1.2d).[5]

The surface of a catalyst nanoparticle is much more complicated. Figure 1.3c and d schematically presents the coexistence of various types of metal atoms and defects. The coexistence of various types of catalytic sites could create different reaction channels leading to different products. The heterogeneity of active sites on a catalyst surface is a factor

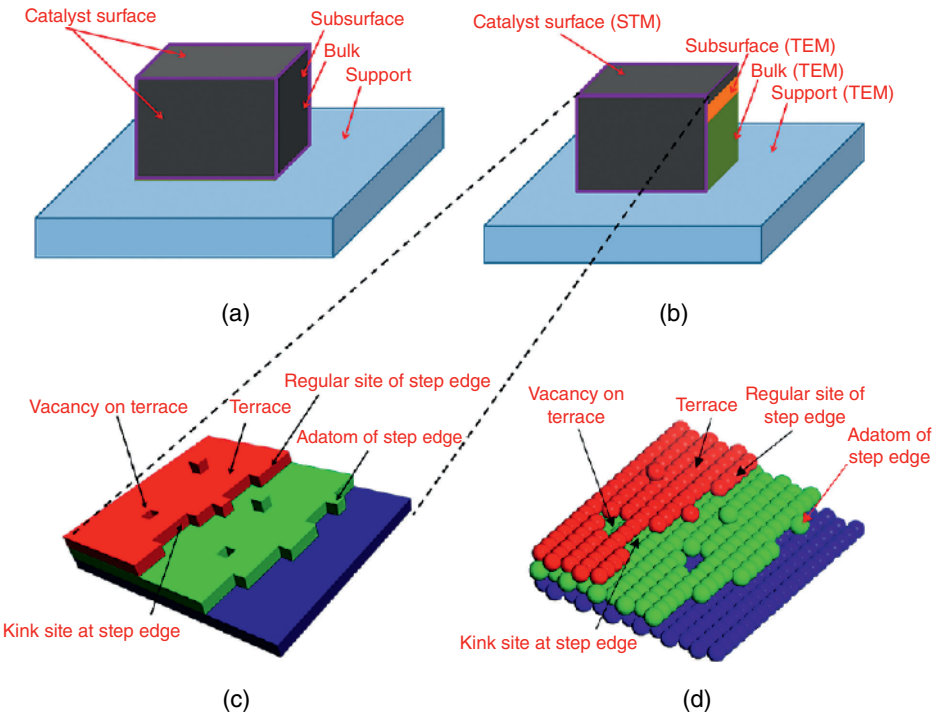

Figure 1.3 Schematics of the structure of a catalyst nanoparticle. (a) Catalyst nanoparticle (gray box) loaded on a support (light blue plate). (b) Surface (gray), subsurface (yellow), and bulk (green) of a catalyst nanoparticle supported on a support; the microscopic characterization techniques of structures of different sections are marked on the schematic. (c) Schematic of a topmost surface of a catalyst nanoparticle consisting of different types of catalytic sites. (d) Schematic of arrangements of catalyst atoms of the topmost surface of a nanoparticle. *Source:* Reproduced with permission from Tao and Crozier[6]/American Chemical Society.

contributing to a relatively low catalytic selectivity for producing an ideal product. Compared to a heterogeneous catalyst, a homogeneous catalyst also known as a molecular catalyst typically exhibits high selectivity for a product since each catalytic site of a molecular catalyst is nearly identical at the atomic level.

The complexity of a catalyst surface is largely enhanced upon considering the factors such as the existence of the second metal, the size-dependent molar fraction of atoms at edge or corner, and the coexistence of cations or anions with different valence states. Each of these factors adds at least one variable, elevating the complexity of a catalyst surface. By adding these variables, a surface has become quite complicated even if the surface is at room temperature in ultrahigh vacuum (UHV). In terms of characterizations of a catalyst surface in UHV, a great number of surface analytic techniques were developed in the past several decades for characterizing a catalyst in UHV environment. X-ray photoelectron spectroscopy (XPS) has been the significantly valuable spectroscopy to identify constituting elements of surface, measure surface composition, and investigate chemical environment of surface atoms. For instance, high-resolution XPS spectrum allows for distinguishing metal atoms with different coordination environments. In addition, scanning tunneling

microscopy (STM) has been the most powerful microscopy to visualize atomic packing of surface at atomic scale. Most of these studies are performed in UHV at cryogenic or room temperature. Obviously, keeping a surface in UHV allows probing a surface readily without any perturbation from an external environment. A significant amount of information on the surface structure, adsorption, desorption, and diffusion was reported in literature in the past decades, which built up the traditional surface science.[2,3] It provides the base for exploring the surface in a complex environment.

Catalysis is performed on a catalyst surface at certain temperature in gas or liquid phase of reactants. We can imagine we have at least two more factors determining the structure of a catalyst surface during catalysis. They are temperature and pressure. Temperature is a necessary factor for most reactions. One reason is that a reaction rate is exponentially increased along the increase of catalysis temperature based on Arrhenius equation regardless of the endothermic or exothermic nature of this reaction; for an endothermic reaction, a high reaction temperature is favorable for a high conversion of reactants or even it is requested for spontaneity of an endothermic reaction. However, the catalysis temperature is a challenging factor for characterizations of a catalyst surface. Unfortunately, with the temperature factor, a catalyst surface at high temperature could be quite different from that at room temperature even if environment of the catalyst is still UHV. For instance, a Rh–Pt alloy surface can restructure to form a Pt-rich surface at high temperature in UHV since Pt atoms have lower surface energy than Rh. Obviously, the temperature factor has driven the segregation of Pt atoms in subsurface or bulk to the surface region since a high temperature can offer Pt atoms in subsurface and bulk enough energy to cross the diffusion barrier of Pt to emigrate and then segregate to the surface of the bimetallic nanoparticle.[7,8]

Another factor resulting in the complexity is the pressure of reactant gas(es). Most of the catalytic reactions are performed in gas phase at ambient pressure or high pressure or even in liquid phase. In such an environment, the molecular density of gas is much higher than that in UHV by at least 13 orders of magnitude. The entropy contribution of the surrounding gas or liquid phase potentially changes the surface structure at an atomic scale. The extent of changing surface structure of the catalyst by the gas or liquid phase is dependent on the original chemical environment of a catalytic site and the pressure, type, and composition of the gas around the catalyst surface while the catalyst is at a constant temperature.

To catalyze a reaction, typically a catalyst must be at room temperature or above in a gas phase at 1 atm or higher or in a liquid phase. Coexistence of the factors of temperature and pressure could largely change the surface structure in an unknown but convoluted manner. This complexity has driven people to study dynamics of a catalyst surface. The formation of such a dynamic surface is typically driven by the catalysis temperature or/and relatively high pressure of reactants; more importantly, in many cases the dynamic surface is maintained by catalysis temperature, type of gas, gas pressure, and composition of the constituting gases of the gaseous environment. In terms of catalysis on catalyst nanoparticles buried in a liquid phase, an expected dynamic surface is a convoluted consequence of catalysis temperature and density, type, and composition of the liquid surrounding the catalyst nanoparticles. Thus, the authentic surface of a catalyst during catalysis needs to be studied in the environment including pressure and temperature at which the catalyst works. The difference between a catalyst surface during catalysis and the catalyst at room temperature in UHV or air is analogous to the difference between on-site track of the living behavior of a

deep ocean fish such as a viperfish and the off-site observation of a dead viperfish on a table.

From the catalyst development point of view, the complexity of the environment-induced dynamic surface of a catalyst has raised a key question, what is the base for the traditional approach of trial-and-error in development of a catalyst. In fact, the complexity of the environment-induced and maintained authentic surface of a catalyst during catalysis undermines the base of trial-and-error approach since the information of catalyst structure a trial-and-error approach typically relies on is mainly obtained through ex situ studies. The high complexity of the catalyst surface under a catalytic condition underlines that development of catalysts needs to rely on environment-induced dynamic surface instead of the surface of an as-prepared catalyst or surface of a used catalyst. A dynamic surface needs to be characterized with in situ spectroscopy or microscopy. One of the powerful in situ spectroscopies is ambient pressure X-ray photoelectron spectroscopy (AP-XPS). It is a surface analytical technique developed from high vacuum X-ray photoelectron spectroscopy (XPS).

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