

# CATALYSIS AND SURFACE SCIENCE

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## 1. Introduction

Catalysis anno 2007 would not be what it is today without the insights obtained from surface science. Owing to this important interdisciplinary field between physical chemistry, solid state physics, materials characterization and spectroscopy we now have a profound insight into the structure of surfaces, the way molecules bind and react, and the role that irregularities such as defects or additional species acting as promoters or poisons may play [1]. Gerhard Ertl's Nobel Prize in Chemistry for his studies of chemical processes on solid surfaces in 2007 acknowledges the importance of the field [2].

In order to realize how surface science can be of help in understanding catalysis, it is useful to consider briefly what the essence of catalysis is. A reaction in heterogeneous catalysis is a cyclic event in which molecules adsorb on the surface, react on the surface and in which finally the products desorb from the surface. The latter is recovered in its original form at the end of the cycle.

The potential energy diagram in Figure 1 explains how a catalyst accelerates the reaction between CO and O<sub>2</sub>, which is important in automotive exhaust catalysis [4] and is usually carried out over a platinum or palladium catalyst. The non-catalytic reaction proceeds when CO and O<sub>2</sub> collide with sufficient energy to overcome the high

activation barrier associated with the splitting of the O-O bond of the oxygen molecule. The catalytic reaction starts by adsorption of the reactants CO and O<sub>2</sub> to the catalyst in a spontaneous reaction. Hence, the free energy is lowered, and because molecules loose entropy when they adsorb, adsorption is by necessity an exothermic process. For most metal surfaces the O<sub>2</sub> molecule dissociates spontaneously upon adsorption (the reason being twofold, first that electron density from the metal fills the anti bonding orbital of the O<sub>2</sub> molecule, and secondly that the bonding of two O-atoms to the surface is energetically more favorable than that of one O<sub>2</sub> molecule). The reaction between O-atoms and CO on the surface of the catalyst is activated, however, with an energy barrier that is significantly lower than for the uncatalyzed reaction. Finally, the product molecule, CO<sub>2</sub>, desorbs from the catalyst in an endothermic step, whereby the surface is free and available for another reaction event.

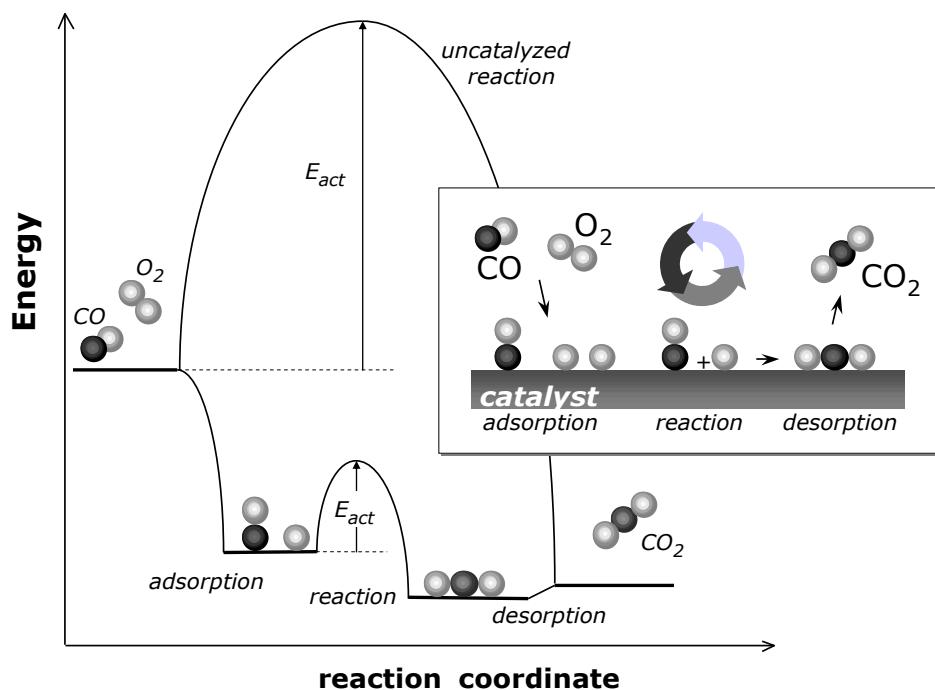


Figure 1. Potential energy diagram for the reaction  $\text{CO} + \text{O}_2 = \text{CO}_2$  showing that the catalytic pathway offers a significantly lower activation energy than the uncatalyzed reaction. The inset illustrates the catalytic cycle: at the end of the reaction the surface is available for the next reaction event (adapted from [3]).

The energy diagram of Figure 1 illustrates several important points:

- The catalyst offers an alternative path for the reaction, which is obviously more complex, but energetically much more favorable.
- As the activation energy of the catalytic reaction is much smaller than that of the uncatalyzed reaction, the rate of the catalytic reaction, being proportional to  $\exp(-E_{act}/k_B T)$ , where  $k_B$  is Boltzmann's constant and  $T$  the temperature, is much larger.
- The overall change in free energy for the catalytic reaction is the same as for the uncatalyzed reaction. In other words, a catalyst changes the kinetics but it cannot change thermodynamics.

- The catalyst accelerates the forward and the reverse reaction to the same extent. Hence a good CO oxidation catalyst can also decompose CO<sub>2</sub> although thermodynamics is usually against such a reaction.
- If the bonding between reactants and catalyst is too weak, or if the catalyst does not split the O-O bond, there will be no conversion to CO<sub>2</sub>.
- If on the other hand the bond between the catalyst and one of the reactants is too strong, the catalyst may be poisoned by (one of) the intermediates, and there will be no reaction.

Hence, for a catalyst to be successful, the interaction between catalyst surface and reacting species should be not too weak, but not too strong either. The essential action of the catalyst lies in breaking the internal bond in at least one of the reacting molecules: A catalyst breaks bonds and lets other bonds form.

## 2. The Role of Surface Science in Catalysis

As the example of the catalytic oxidation of CO illustrates, all the action in the catalytic cycle happens at the surface of the catalyst: adsorption, dissociation, reaction and desorption. Surface science is a discipline in which all these phenomena can be studied in great detail and under conditions which are well controlled:

- Surfaces are usually those of single crystal materials, such that at least at the start of an experiment the structure of the surface is known in atomic detail (although defects may have serious disturbing effects)
- Experiments are usually carried out in ultrahigh vacuum, such that surfaces are empty unless gases are admitted onto the surface on purpose.
- As surfaces of single crystals are flat and visible from the outside world, as opposed to technical catalysts which contain small particles inside porous supports, many experimental methods are available that cannot be used (or not to their full potential) on technical catalysts.
- Because of the defined and periodic nature of surfaces, experiments from surface science are eminently suitable for modeling by computational chemistry. The combination of these two disciplines has provided indispensable insight into catalytic phenomena [3,5,6].

In addition to the successful contribution that studies on single crystal surfaces have made to understand the fundamentals of catalysis, surface science has become increasingly successful in studies of supported particles as well [7]. In such studies the porous oxide or carbon support is replaced by either a single crystal oxide or graphite, or by a thin film oxide on top of e.g. a silicon wafer. Catalyst particles can be applied in several ways, e.g. by evaporating metals, by chemical vapor deposition or atomic layer epitaxy, or by wet chemical impregnation and grafting [8].

Figure 2 schematically summarizes the two approaches taken in the application of surface science in catalysis.

The fact that surface science experiments are usually carried out under ultrahigh vacuum implies that catalyst surfaces are studied under different conditions than under which they operate in chemical processes. Translating results obtained under vacuum to

the situation in the real world is far from trivial but these bridging the gap strategies fall outside the scope of this chapter unfortunately.

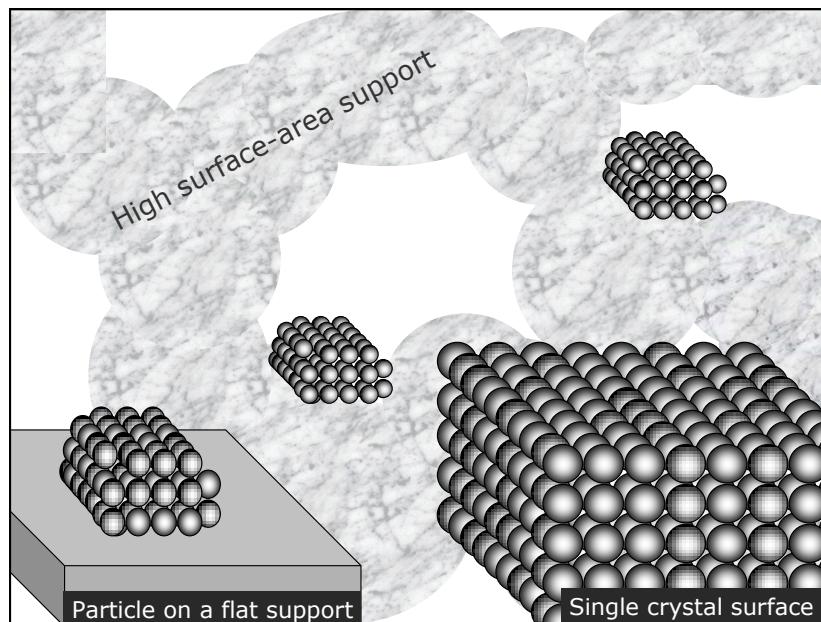


Figure 2. Technical catalysts consisting of small particles on a high surface area support can be modeled in surface science by the almost perfect surfaces of single crystals or by depositing small particles on flat model supports (adapted from [3]).

### 3. Tools of Surface Science

In order to record exactly what the state of a catalytic surface is, we need techniques that reveal the structure, the composition and the morphology of the surface, as well as the identity, position and geometry of adsorbed species, all preferably at atomic-scale resolution. In addition we need time-resolved methods to study the kinetics of dynamic phenomena such as adsorption, sticking, reaction, ordering, and desorption.

Characterization techniques [9-11] become surface sensitive if they are based on particles or radiation that have low penetrating power (i.e. on the order of a few atomic layers), or if they concentrate on species, geometries or environments that are exclusively present on the surface. Electrons of low energy have inelastic mean free paths on the order of a few nanometers, and therefore spectroscopies such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) or diffraction methods such as Low Energy Electron Diffraction are important surface sensitive tools in the study of single crystals and planar model catalysts [9]. Also methods based on the scattering of low energy ions with surfaces are highly surface sensitive, particularly because ions that penetrate the solid and scatter off deeper layers are usually neutralized and cannot be detected when they reach a detector [10]. Vibrational methods such as electron energy loss spectroscopy, reflection absorption infrared spectroscopy or sum-frequency generation detect molecules or fragments on the surface, whereas temperature programmed techniques rely on desorption of molecules from the surface when the temperature is increased [11].

Surface Science Tools in Catalysis Research			
Acronym	Full name	Principle	Information
AES	Auger Electron Spectroscopy	Energetic electrons create core-holes in the atomic orbitals; these are filled by the Auger decay process in which also electrons are emitted at characteristic kinetic energies	surface chemical composition
AFM	Atomic Force Microscopy	A nanometer sized tip on a flexible cantilever scans the topology of a surface; the deflection of the cantilever is usually read out by optical means and is calibrated by piezo controlled movements of the surface; generally applicable on all surfaces	surface morphology
EELS	Electron Energy Loss Spectroscopy	Monochromatic electrons excite vibrations or electronic excitations at the surface; the associated energy loss is measured and equals the vibrational energy or the electronic transition energy	vibrations of adsorbates; surface phonons; electronic properties
FEM/FIM	Field Emission Microscopy/Field Ionization Microscopy	The tip of a metal is imaged by the electrons that are emitted from the tip under a strong electric field; the image is obtained on a fluorescent screen; FIM utilizes a low pressure rare gas such as helium to create ions at the tip, which are then accelerated towards the fluorescent screen.	surface structures in atomic detail
ISS	Ion Scattering Spectroscopy	Ions of fixed energy collide with the surface and loose energy to atoms dependent on their mass; the energy spectrum of backscattered ions represents a mass spectrum of the surface	surface composition
LEED	Low Energy Electron Diffraction	Low energy electrons scatter from a surface; due to the wave character of the electrons an interference pattern of bright spots arises which represents the reciprocal lattice of the surface	periodic surface structures
RAIRS	Reflection Absorption Infra Red Spectroscopy	An infrared beam impinges under glancing angle on a surface; adsorbed molecules absorb infrared photons of characteristic wavelengths	vibrations of adsorbed molecules
RBS	Rutherford Backscattering Spectrometry	High energy ions penetrate into the target and scatter back from a variety of depth thus creating a mass spectrum which also contains depth selective information	surface composition and concentration depth profiles
SFG	Sum Frequency Generation	Non linear optical process in which infrared light of variable wavelength is mixed with green light of fixed wavelength and scatters at surfaces; adsorbed molecules absorb and scatter, while the light beams add up to blue; the process is extremely surface sensitive as the selection rules require a strict non-centro symmetric geometry.	vibrations of adsorbed molecules
SIMS	Secondary Ion Mass Spectrometry	Primary ions impinge on a surface where they stimulate the emission of surface fragments which reveal structures present on the surface; if the secondary species are ions, they are efficiently detected with a mass spectrometer; the technique is highly sensitive but difficult to quantify.	surface composition; trace analysis
STM	Scanning Tunneling Microscopy	Based on the electric tunneling current that flows between a nanometer sized tip and the surface, STM measures a convolution of the electron density of states at the tip and the surface, which resembles the topography; the sample must be conducting	atomic scale morphology (albeit indirectly via the electron density)
TPD	Temperature Programmed Desorption	An adsorbate covered surface is heated while the desorption of the adsorbate is measured with a mass spectrometer; can also be used to study reactions between coadsorbed species, provided the product desorbs instantaneously;	adsorbate coverages; heats of adsorption; activation energies
XPS/ UPS	X-ray or UV Photoelectron Spectroscopy	Photons (X-ray or UV) are converted via the photoelectric effect to electrons, of which the kinetic energy is measured. The difference between photon energy and kinetic energy is the binding energy of the electron to the atom from which it originates, and therefore element specific.	surface composition; oxidation state; electron density of states

Table 1. A brief overview of the most common methods in catalytic surface science.

Scanning probe microscopy relies on the short ranged interaction between an atomically sharp tip and the atoms in the surface [12]. These methods have given indispensable insight in morphology on a local scale, and have made us aware that surfaces are seldom the idealized structures that we like to have in mind when we plan our experiments. Table 1 gives a brief overview of the most common methods in catalytic surface science. More detailed information can be obtained elsewhere in this encyclopedia or in standard textbooks [9-12].

#### 4. The Structure of Surfaces

The important catalytically active metals are found in Group VIII and I-B of the Periodic Table. Most of these metals have a face-centered cubic structure (fcc: Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au), some are hexagonally close-packed (hcp: Co, Ru, Os) and one is body-centered cubic (bcc: Fe). Figure 3 presents the most stable surfaces that these crystals expose. Of course, many more surfaces can be cut from crystals, with steps, if the surface orientation remains parallel to one of the major axes, or with steps and kinks otherwise.

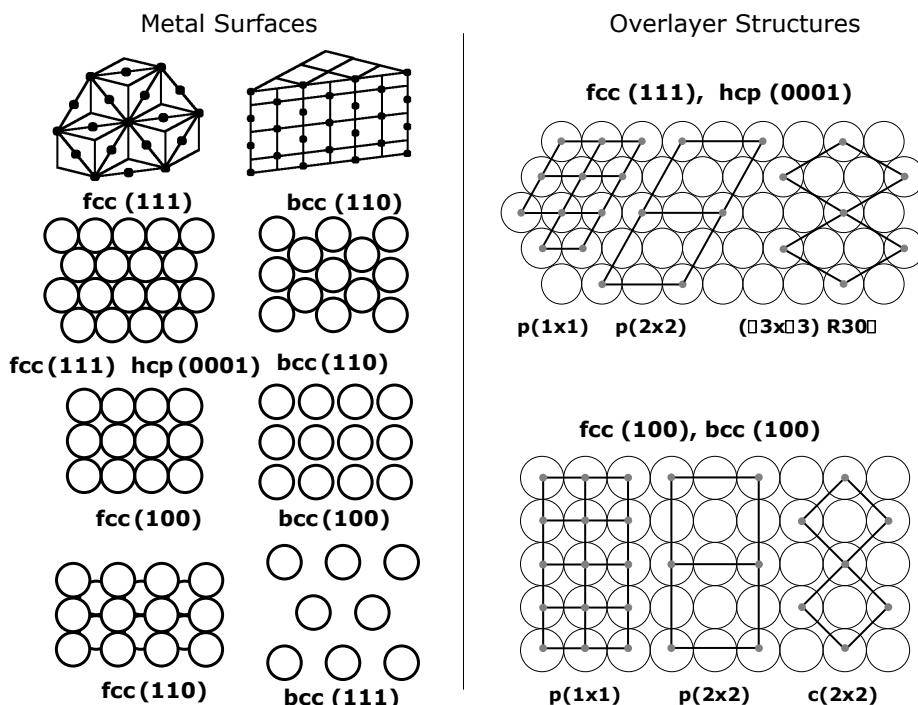


Figure 3. Surface structures of the face and body centered cubic metals, and examples of overlayer structures in Wood's notation

The reactivity of a particular surface depends on the number of bonds per surface atom that had to be broken in order to create the surface. Consider for instance the fcc structure in Figure 3, where every atom inside the crystal has twelve neighbors. To create the fcc (111) surface, three neighbor atoms had to be removed for every surface atom, while six neighbors are still present in and three just below the surface. An atom in the fcc(100) surface, however, has four neighbors in and four below the surface, and misses four neighbors which were taken away when the crystal was cut. Hence, atoms in the fcc (100) surface have a lower coordination than in the fcc (111) surface, and hence they are more

reactive. Therefore, atoms such as carbon and nitrogen generally bind stronger to fcc (100) than to (111) surfaces (for molecules such as CO this is not necessarily the case as we see later).

The surfaces in Figure 3 represent the ideal termination of the bulk structures. Very often, however, the atoms relax, or restructure, to minimize the surface free energy. Generally atoms will be slightly displaced from their ideally bulk-truncated sites in the direction perpendicular to the surface, but rearrangements in the plane of the surface, called reconstructions, may occur as well, particularly in the case of the more open surfaces such as the fcc (110).

Ideal surfaces possess periodicity in two dimensions. Hence, two base vectors define the unit cell of a surface. Adsorbates often form ordered overlayers with their own periodicity, see Figure 3 for some examples. The structure of these adsorbate layers is given in Wood's notation, which merely indicates the size and orientation of the overlayer unit cell with respect to the substrate. For instance, the notation Rh (100) - c(2x2) O indicates that oxygen atoms form an ordered layer with a unit cell that has twice the dimensions of the Rh (100) unit cell, with an additional O in the centre. Note that this abbreviation does not specify where the adsorbate is with respect to the metal atoms. It may be on top, in bridged or in fourfold sites, or in principle anywhere as long as the periodic structure is c(2x2) with respect to the underlying surface.

Oxides are made up of positive and negative ions and exhibit surfaces that may be polar, or overall neutral [13]. Oxide surfaces are much less reactive than metal surfaces. Cations at the surface possess Lewis acidity, implying that they behave as electron acceptors. The oxygen ions behave as proton acceptors and are thus Brønsted bases. Often the reactive sites are associated with defects, such as oxygen vacancies. In the rest of this chapter we limit ourselves to metal surfaces.

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