

# Chemistry of bimetallic surfaces\*

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Chemistry of bimetallic systems is currently the topic of interest in surface and catalytic science. A number of interesting phenomena such as segregation, faceting, reconstruction and chemical oscillations, which have direct correlation with the atomic scale modifications of these surfaces are emerging in this field. Bimetal single crystals and bimetallic overlayers fabricated on metal substrates are being used to investigate the properties of bimetal surfaces by employing surface spectroscopic techniques such as AES, XPS, LEED, LEIS, and STM. Some of these studies are concerned with the heteronuclear metal-metal bond present in the top surface layers. The surface structures impart unusual chemical and catalytic properties to bimetallic systems. This article reviews the current understanding of the topic, highlighting the preparation methods of mono and multilayer binary alloy surface phases, and various investigations on physical and chemical phenomenon occurring on them. It also touches upon the chemisorption and catalytic properties of these fascinating bimetal surfaces.

THE surface and interface chemistry of 'mixed metals', in general, and bimetallic alloys, in particular, is an important subject for a number of technological reasons<sup>1-7</sup> some of which are: (i) corrosion resistance and hardening; (ii) catalyst chemistry; (iii) metal-metal interfaces; (iv) microelectronics fabrication; (v) electrochemistry; and (vi) surface magnetic films.

The resistance to corrosion and wear is determined by the surface chemical properties and can be influenced by using proper metal components and varying their concentrations. In catalysis, the addition of second metal to the conventional metal particle may generate an alloy whose surface may exhibit potentially unique catalytic properties. For this reason, many of the bimetallic catalysts have been in the focus of scientific and technological interest<sup>2</sup>. The metal/metal interface studies have also been carried out to understand the alloying processes on the top layer of magnetic films<sup>6</sup>. Surface alloying has been investigated on nonmagnetic materials for surface ordering and reactivity. The advent of scanning tunneling microscopy (STM) has made it possible to examine electro-deposited metallic layers *in situ*<sup>7</sup>.

## Chemistry of bimetallic surfaces: Heterogeneous catalysis

In this article, we shall focus on the chemical concepts of bimetallic surfaces and their relevance mostly to heterogeneous catalysis. Recently, the role of 'chemical promoter' in catalysis has acquired significance<sup>8</sup>. A promoter can be a metal or an oxide added to a catalyst component to increase its catalytic activity or selectivity. For example, the well-known ammonia synthesis catalyst, and the automotive three-way catalysts use potassium and ceria, respectively, as promoters. Nevertheless, there is a need to investigate multi-component catalysts as potential substitutes for the traditional catalytic materials. The logical step is the extension of surface chemical studies to bimetallic and tri-metallic surfaces in order to understand and evaluate their chemical and catalytic properties.

Figure 1 shows the examples of four different fcc(100) surfaces. The first one has 100% metal X (Figure 1 a). The next two surfaces have 50% of the component X and 50% of the component Y with different arrangements of the atoms X and Y (Figure 1 b, c). The last one has a surface with 75% X and 25% Y. It is important to examine how the chemical nature, orientation, thermal and chemical stability and binding energy of an adsorbed species vary on these different surfaces. This information will help in the understanding of catalytic reactions, since the reactants are adsorbed and then transformed into products on the surface itself.

A small change in the surface structure or in the chemical environment of an adsorbed precursor can result in drastic changes in the catalytic behaviour, such as selectivity or activity for a given reaction. The nature and identification of reaction sites is an important prerequisite for understanding chemical processes, and for

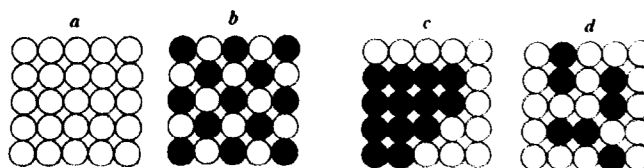


Figure 1. A hypothetical situation of (100) surfaces of an alloy XY with the fcc structure. (a) pure X; (b) 50% X, 50% Y, ordered; (c) 50% X, 50% Y, with clustering of Y; (d) 75% X, 25% Y. From ref. 3.

\*This article is dedicated to Professor C. N. R. Rao.

designing new functional bimetallic catalyst surfaces. Therefore the following aspects of an alloy surface should be examined somewhat closely: (i) The chemical composition of an alloy surface. (ii) The surface structure factor. (iii) The electronic structure and geometric factors.

### *The chemical composition of an alloy surface*

For adsorption and chemical properties of surfaces, the composition of the outermost layers and, to some extent, the layers immediately below the surface are of crucial importance. An important phenomenon that occurs on alloy surfaces is the segregation by which the surface chemical composition is completely modified. Some of the factors affecting the surface segregation of an alloy XY are; the differences in bond strengths (X-X, X-Y and Y-Y), atomic size, enthalpies of sublimation, and surface energies<sup>9</sup>. One representative example is CuNi bimetallic system. There is a substantial surface Cu segregation occurring on clean  $\text{Cu}_{0.5}\text{Ni}_{0.5}$  system as proved by Auger electron spectroscopy (AES) and Low energy ion scattering (LEIS) methods<sup>10</sup>. The Auger spectra of  $\text{Cu}_{0.5}\text{Ni}_{0.5}$  alloy sample are reproduced in Figure 2.

The Auger peaks around 100 eV are sensitive to detect Cu segregation in the top surface layers. The spectrum (a) shows the Auger peak of Cu alone at 106 eV on clean and annealed  $\text{Cu}_{0.5}\text{Ni}_{0.5}$  alloy surface, while spectrum (b) from sputtered  $\text{Cu}_{0.5}\text{Ni}_{0.5}$  sample indicates the presence of both Cu and Ni on the surface. When the sputtered sample is annealed, Ni signal at 100 eV disappears, thereby indicating complete segregation of Cu on the surface. The gas-induced surface segregation of Ni, instead of Cu, has been reported<sup>11</sup> on  $\text{Cu}_{0.5}\text{Ni}_{0.5}$  alloy supported on  $\text{SiO}_2$  when exposed to CO and hydrogen gases. The reversal of segregating component is due to the stronger chemisorption bonds that can form between Ni and the adsorbates. Therefore gases such as CO can extract subsurface Ni atoms leading to selective Ni segregation on the surface.

### *The surface structure factor*

The surface structure of a metal influences its adsorption behaviour. This is because the heat of adsorption or dissociation probability of adsorbed gas molecules is different on different single crystal faces of a pure metal. It tends to be more complicated for alloy faces<sup>8</sup>. On a 100% pure fcc(100) surface of a metal X (Figure 1a), a simple diatomic molecule like CO or NO can have the choice of quadruplet, doublet or singlet sites available for chemisorption. The nature of adsorbed species and the associated heat of adsorption differ significantly on these adsorption sites. Similarly the

atomic ordering pattern for the components X and Y is considerably different in Figure 1b, 1c and 1d. Obviously, the adsorption sites available on these surfaces are quite different, and it is important to know the atomic arrangement of the two components on the surfaces.

### *The electronic structure and geometric factors*

The electronic structure of the active metal is somewhat dependent on its chemical environment. When the active component X is alloyed with Y, the intrinsic activity of the metal atoms on the surface will be modified. The change in binding energy of a surface atom X, when it is surrounded in part or totally by Y atoms instead of X atoms exclusively, is termed as ligand (electronic) effect. The changes in the heat of adsorption due to alloying of one metal with another often indicate the ligand effect. The addition of a second metal can produce dramatic changes in the selectivity of a reaction. This is mainly due to dilution effect on the active ensemble of metal atoms on the catalyst surface. However, reactions that occur on single atom sites, rather than on an ensemble, do not get affected until the active metal is completely replaced by the inert metal. This is called ensemble (geometric) effect. These are well-known concepts proposed in catalytic science. As an example, modification of an active Group VIII transition metal with Group 1B metals significantly suppresses the catalytic activity for hydrocarbon reactions which require

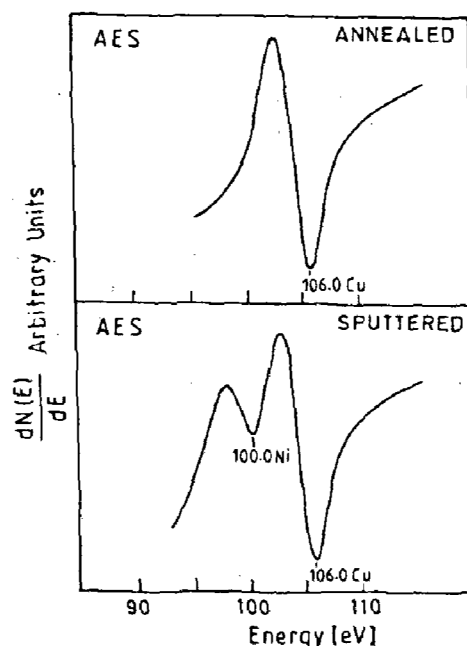


Figure 2. Auger spectra of  $\text{Cu}_{0.5}\text{Ni}_{0.5}$  alloy sample showing Cu segregation on annealed surface. Sputtering exposes the bulk Ni. From ref. 10.

large ensembles of surface atoms<sup>12</sup>. The effect of adding copper to nickel catalyst is shown in Figure 3.

Nickel is an active metal for both ethane hydrogenolysis and cyclohexane dehydrogenation reactions. However, addition of copper selectively decreases the rate of ethane hydrogenolysis, while the rate of cyclohexane dehydrogenation remains constant until the copper content is quite high. The results in Figure 3 indicate that ethane hydrogenolysis reaction is promoted by ensembles of Ni atoms of critical size. The addition of copper dilutes the nickel on the surface and decreases the number of such ensembles available for this reaction. The rate of cyclohexane dehydrogenation is not influenced by copper addition, because this reaction takes place presumably on single Ni atom sites that decrease only at high copper coverage. The incorporation of copper in nickel could also change the density of states of the d-band and hence the local electronic character of the active site. Such changes in the local electronic structure due to alloying may influence the electron transfer between the adsorbate molecule and the bimetallic substrate. This will finally be reflected in the reactivity of the adsorbed molecules and hence the reaction characteristics. While it is difficult to establish the influence of electronic structure changes on the activity of CuNi system, the ensemble effect is clearly discerned. Thus the change in activity and selectivity of CuNi alloy is primarily due to the variations in the surface concentration of Ni. The various aspects mentioned above could be inter-related, and should be examined carefully while investigating different alloys systems.

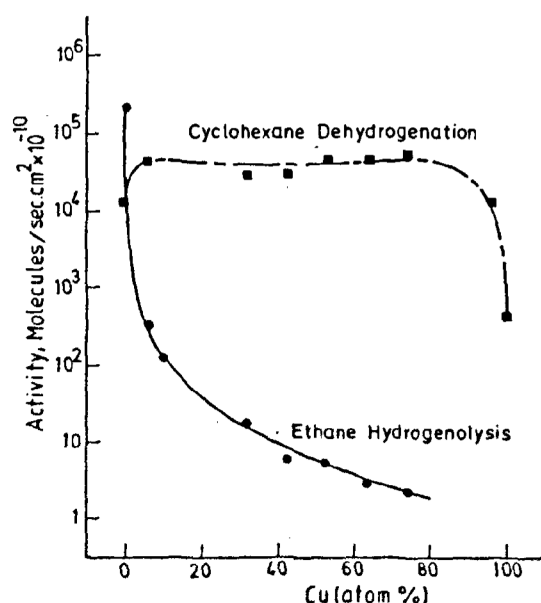


Figure 3. Activity of CuNi alloy catalyst for hydrogenolysis and dehydrogenation reactions at 589 K. From ref. 13.

## Preparation methods

Having introduced why and how the bimetallic surface chemistry is studied, particularly in relation to catalysis, the general preparative methods of these surfaces are next described.

Bulk single crystal alloys can be prepared commonly by melting the metal components X and Y together, and then using zone refining to obtain single crystal material. The alloy surface can then be prepared carefully by cutting a single crystal rod of an alloy in the desired orientation.

Surface alloys can also be prepared by deposition of atoms of the component X onto a metal surface of the component Y. Here the surface atoms of the substrate Y provide one of the elements of the surface alloy. Surface alloys thus prepared differ from bulk alloy surfaces because mixing of the atomic species is confined to a single or a few atomic layers. This type of two-dimensional alloys can also be prepared by evaporating metals X and Y on to a third, chemically different, substrate. If the two deposited elements mix on the surface and do not diffuse into the substrate, a surface alloy layer could be formed. Mixing at atomic scale may occur during deposition, or can be achieved by successive thermal treatment. These ultrathin epitaxial films exhibit novel chemical properties.

## Ultra-high vacuum methods to study bimetallic surfaces

Bimetallic surfaces have been studied by surface crystallographic techniques, requiring ultra-high vacuum conditions, that is at residual pressures lower than approximately  $10^{-10}$  Torr. Under these conditions, a metallic surface can be cleaned and maintained in this condition for hours. Furthermore, the vacuum condition allows the use of charged particles (ions or electrons) as probes. Vacuum is not required for scanning probe methods (e.g. scanning tunneling microscopy, STM) or photon-based techniques (e.g. X-ray diffraction), and, hence, surface studies may also be performed in air or solution. However, it is not possible to study atomically clean metal surfaces in these conditions.

In most cases UHV studies require single crystals, although polycrystalline samples can be used as well. Once in vacuum, the sample can be cleaned by noble gas ion ( $\text{Ar}^+$ ) bombardment. This method may cause significant alteration in the surface composition of an alloy due to preferential sputtering (different removal rate of atoms of different mass). Usually, a thermal treatment is required to bring the surface back to the equilibrium composition.

Spectroscopic methods such as AES and X-ray photoelectron spectroscopy (XPS) are capable of

determining the chemical nature and composition of one or two layers of the alloy surface<sup>14</sup>. On the contrary, real space methods<sup>15</sup> have a great potential and the atomic resolution of STM gives access to the two-dimensional atomic distribution in the surface layer. STM can be used to determine the surface parameters as well.

Surface composition and structure may also be determined using noble gases or alkali ion scattering. LEIS (0.1–10 keV) is a surface analysis technique which selectively probes the outermost atomic layer of a solid<sup>16</sup>. In the most straightforward applications such as alloy surfaces, the technique gives quantitative information about the elements present on the alloy surfaces and its top layer composition. This technique is somewhat insensitive to the chemical nature of the surface atoms. The extreme sensitivity of LEIS to the outermost atomic layer makes it an useful tool for investigating surface segregation and adsorption<sup>17,18</sup>. A typical LEIS spectrum of dilute Pd<sub>5</sub>Fe<sub>95</sub> binary alloy is shown in Figure 4. The spectrum was recorded on the alloy sample equilibrated at 870 K for five minutes, using <sup>4</sup>He<sup>+</sup> primary ions of 1.0 keV kinetic energy. The two peaks observed are due to the backscattered ions by surface Fe and Pd atoms as indicated in the figure. The spectrum unequivocally exhibits higher Pd scattering intensity than expected from the alloy composition. This suggests that large amount of Pd is segregated in the outer layer of the alloy surface. Taking the relative sensitivity factor  $S_{Pd/Fe} = 2.4$ , the Pd concentration in the outer layer is estimated to be about 65 Pd at%.

Low energy electron diffraction (LEED) is an important technique to determine the atomic arrangement on carefully prepared single crystal alloy surfaces. Photoelectron diffraction is another recent technique<sup>15</sup> which is based on the scattering process that an emitted electron undergoes when interacting with the atoms around the emitter. Interference effects cause a variation in the

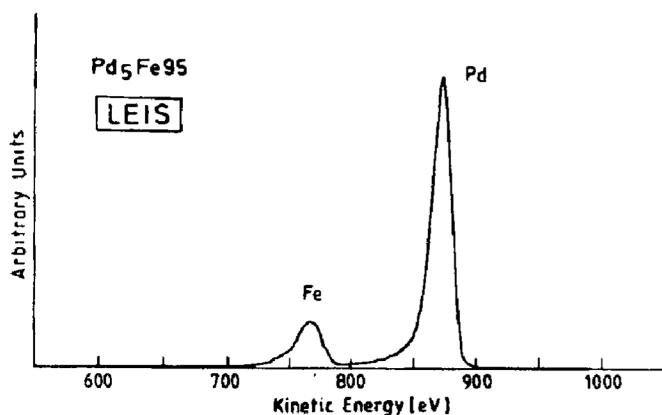


Figure 4. LEIS spectrum of Pd<sub>5</sub>Fe<sub>95</sub> binary alloy stabilized at 870 K, showing substantial Pd segregation in the surface layer. From ref. 18.

intensity of electron emission as a function of angle or energy. By measuring this variation, it is possible to obtain information about the local structure. This technique can be applied for studying multicomponent alloy systems as well as adsorbed species on them. All the methods described above have been used to study alloy surfaces of different compositions and structure. However, it is important to note that every technique provides only limited information and complete picture of a bimetallic surface can be obtained only when several surface techniques are employed simultaneously.

## Binary alloy systems

A number of binary alloy systems have been studied in the literature. The details of preparation methods and characterization of binary alloys, using various spectroscopic techniques have been summarized in earlier reports<sup>1,19,20</sup>. The work so far has been confined relatively to binary metal systems and not ternary or higher systems. Some of the important alloy systems in catalytic

Table 1. Partial list of binary alloy systems examined in catalysis

Reaction	Alloy systems	Ref. no.
CO oxidation	Cu–Cr	21
	Pt, Pd and Rh alloys	22
Dehydrogenation	Ni–Cu	13
	Ni–W	23
	Ni–Sn	24
	Pt–Co	25
Acetylene cyclotrimerization	Pd alloys	26
Fischer–Tropsch synthesis	Ru–Group IB alloys	27
	Fe–Ru, Fe–Ni, Co alloys	22
Exhaust emission conversion	Pt–Rh or Pd	28
Olefin hydrogenation	Pd–Ti	29
	Pd–Cu, Sn or Fe	30
	Pd–Fe	18
	Pd–Co	31
Hydrocarbon reactions	Ni, Pt, Pd, Ru based alloys	32
Reforming	Pt–Re, Pt–Ir, Pt–Au	33
	Pt–Sn, multimetallic cocktails	22
CO methanation	W–Ni and Co; Ru–Cu	34
	Ce based intermetallics	35
Alkane hydrogenolysis	W–Ni, Pt–Ni, Pt–Re, Ru–Cu	34
Hydrodesulfurization	Co–Mo, Ni–Mo	36
Hydrodenitrogenation	Ni–Mo	37
Hydrogenation of edible oils and fats	Ni and Ni based alloys	38

work are presented in Table 1. These alloy systems can be in the form of supported particles, powders, surface films, polycrystalline or oriented single crystal bulk specimens and epitaxial layers. The preparation methods, evaluation of structure, and reactivity of various supported bimetallic catalysts have been reviewed<sup>1,4</sup>. In the following sections, we restrict the discussion to model surfaces under closely related headings – alloy surfaces and surface alloys – for convenience.

### *Alloy surfaces*

As mentioned earlier, alloy surfaces are prepared from bulk single crystal alloy samples. The alloys for which surface structure data are available presently, belong either to fcc or to bcc phases (Figure 5). In many cases, the surface unit mesh is reported to be same as expected from truncation of the bulk lattice. In these cases, the structure of the outermost surface layer is often the same as bulk crystallographic plane with the same indices (Figure 6).

For ordered alloys, outward atomic relaxation with respect to surface plane is also possible in some cases. It should be noted that an experimental observation of a LEED pattern corresponding to bulk termination does not imply absolute determination of the surface structure. In ordered intermetallic compounds, the bulk termination model is not normally straightforward, since the planes stacked along a specific crystallographic direction do not necessarily have all the same composition. These considerations are also applicable to alloys with the bcc type structure (Figure 5). It is therefore possible that the composition of the topmost layer of an ordered alloy need not be the same as the bulk phase. In such a situation, the observed surface structure could still be taken as bulk termination, since the difference in composition is not the result of surface segregation. It is also reported that when there is a choice between a mixed and a pure surface termination of an ordered bulk alloy, the mixed termination is preferred.

In random substitutional alloys as well, the LEED

pattern observed corresponds to bulk truncation. This does not mean that the surface structure and composition correspond exactly to that of a bulk plane with the same indices. A strong enrichment of one of the components is normally observed on the surface. This is more pronounced in Pt-based alloys where Pt concentration is higher in the top layers. Surface reconstruction, that is a surface atomic mesh which is not the same as the bulk atomic mesh along surface plane, has been observed for many alloys. This phenomenon is observed when the termination of an alloy surface is a mixed plane. In this case reconstruction leads to the formation of ordered, single layer alloy phases. Some of the cases reported are related to topmost layers of hexagonal symmetry on the (111) surface of fcc alloys. For example, the ordered Pt<sub>3</sub>Sn alloys<sup>39</sup> have two possible terminations, one of which has a  $(\sqrt{3} \times \sqrt{3})$  R30° periodicity as shown in Figure 7.

This structure has maximum number of in plane heterogeneous bonds. The Sn–Sn bonds are energetically less favourable than Sn–Pt bonds and this structure is formed at low tin concentration. This kind of reconstruction may occur more in dilute alloys.

We can also expect defects and disorder on alloy surfaces. STM has the unique capability of imaging these defects in real space. It is possible to observe the step distribution and height on the surface using STM. In the case of Co/Cu(100) interface, STM study shows that the diffusion of metal atoms in the surface region at low temperatures is due to the presence of defects, such as the ‘pinholes’<sup>40</sup>.

### *Surface alloys*

The term ‘surface alloy’ refers to samples in which alloying occurs only on the surface region. There are two cases to be considered: (i) single atomic layer binary alloy (ii) multilayer surface alloy phases (also called as epitaxial alloys). Both single layer and multilayer alloys have been prepared by depositing one metal on the surface of a second metal and their subsequent interdiffusion resulting from annealing. A number of proven examples where the formation of either single atomic

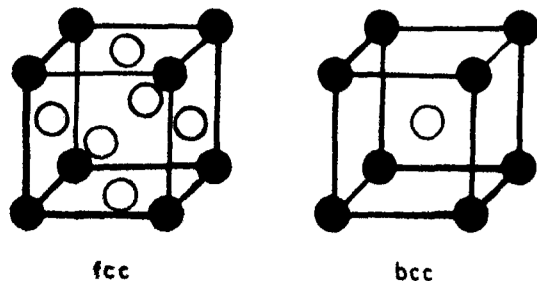


Figure 5. The ordered bulk structure of fcc and of bcc alloy lattices. Surfaces of binary alloys which crystallize to these two lattices are well studied. From ref. 19.

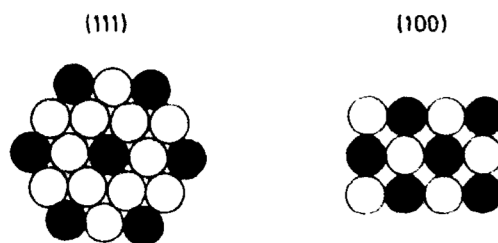


Figure 6. Bulk truncation models for the surface structure of the (111) and (100) of ordered Cu<sub>3</sub>Au type fcc alloys. From ref. 19.

layer surface alloy or multilayer surface alloy formed by diffusion have been compiled in ref. 19. The typical example of a surface alloy is Sn-Pt that forms when Sn is deposited on Pt(111) surface. The preparation of these surface alloy phases should necessarily be done in clean UHV environment, using pure metal sources.

**Monolayer surface alloy phases:** The process of formation of these phases seems to be the same as discussed before. In a number of systems, the alloy phase is confined to the first atomic plane only and alloying does not spread significantly to the underlying layers (Figure 8). These monolayer phases maintain their structure under extended annealing, and are thermodynamically stable. They contain maximum number of heterogeneous pairwise interactions. Qualitatively, such phases are stabilized by a strong intermetallic bond and hence occur for elements which form ordered bulk alloys with a negative enthalpy of formation. However, there are exceptions where single layer alloy phases form among elements that do not mix in bulk<sup>41</sup>. The research in this field of single layer surface alloys is rapidly increasing. The existence of these monolayer alloy phases is explained as a balance between two opposing tendencies, namely maximizing the number of energetically favourable intermetallic bonds and minimizing surface energy. The maximization of the number of bonds, alone, would lead to long-range bulk diffusion and to the formation of a dilute bulk alloy. However, accommodating the minority component within the top most surface layer may be energetically favourable for relieving strain effects due to size differences.

**Multilayer surface alloy phases:** A surface alloy phase of several atomic layer thick may be formed by annealing simultaneously the metal substrate on which the other metal atoms are being deposited. Interdiffusion would lead to the formation of surface alloy phase (Figure 9). The formation of such an ordered, epitaxial multilayer phase has been observed experimentally in Sn/Pt(111) (ref. 42). Figure 10 illustrates the top view schematic drawing of the surface atomic structure and the corre-

sponding LEED pattern for clean Pt(111) hexagonal surface and the  $(2 \times 2)$  and  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  Sn/Pt(111) surface alloys. The clean Pt(111) crystal has an hexagonal  $(1 \times 1)$  surface which does not exhibit surface reconstruction (Figure 10 a). The ordered surface alloys showing  $(2 \times 2)$ , and  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  LEED periodicity can be prepared by evaporating respectively 0.25 and 0.33 monolayers of Sn on clean Pt(111) surface, and subsequently annealing the sample to around 1000 K for 10 s. The observed  $(2 \times 2)$  pattern indicates an ordered substitution of the Pt atoms by Sn atoms, leading to (111) face of  $Pt_3Sn$ . However, at higher coverage of Sn, the surface alloy phase showing  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  periodicity is assigned to a substitutional surface alloy of composition  $Pt_2Sn$  (ref. 39, 42).

Many metal/metal systems also exhibit this phenomenon of multilayer alloying and, in particular, rare earth films deposited on transition metal substrates. For example, Ranga Rao *et al.*<sup>43,44</sup> recently studied Sm/Ru(001) system, using XPS. These studies show that the deposition of Sm on Ru(001) at 500 K leads to the growth of an ordered Sm monolayer initially. At the completion of one monolayer Sm, interdiffusion sets in leading to the formation of an alloy monolayer, and then to the growth of a thick intermetallic alloy phase on the surface. The evidence of alloy formation is obtained directly from Ru 3d XPS photoemission lines as shown in Figure 11. The surface alloy phase is correlated to the hexagonal type intermetallic compound,  $SmRu_2$ . Interfacial studies have also been carried out on transition metal substrates of polycrystalline nature<sup>45</sup>.

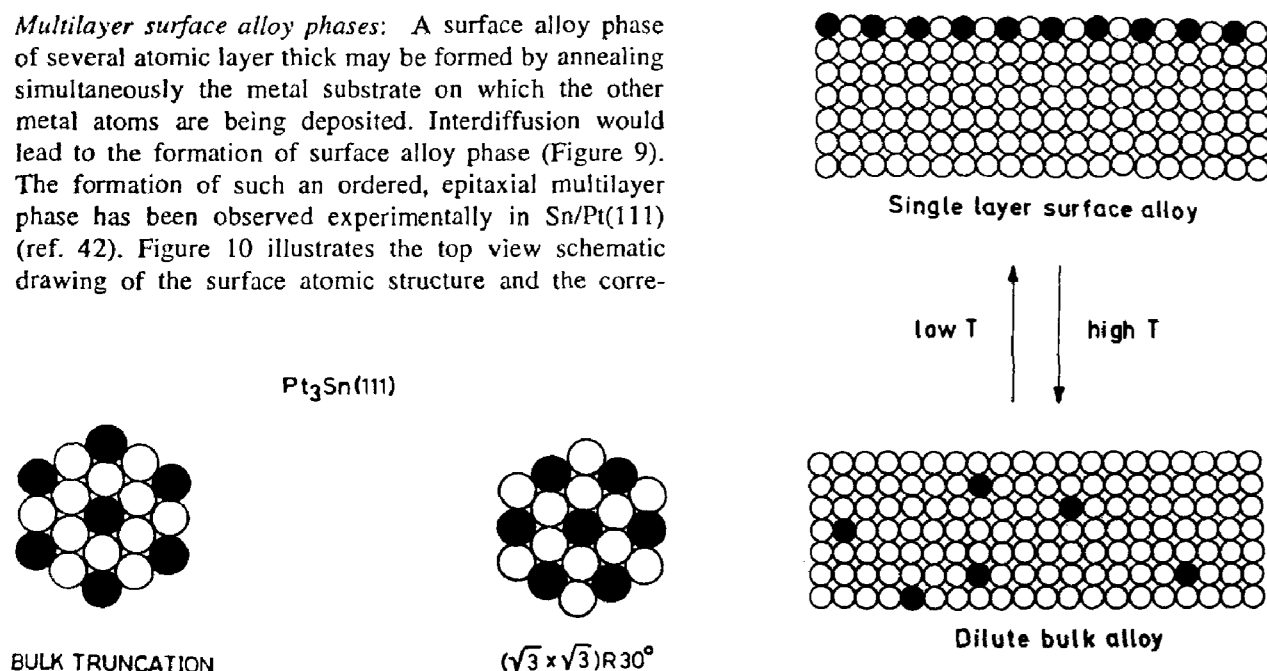


Figure 7. Surface reconstruction of ordered alloys. From ref. 19.

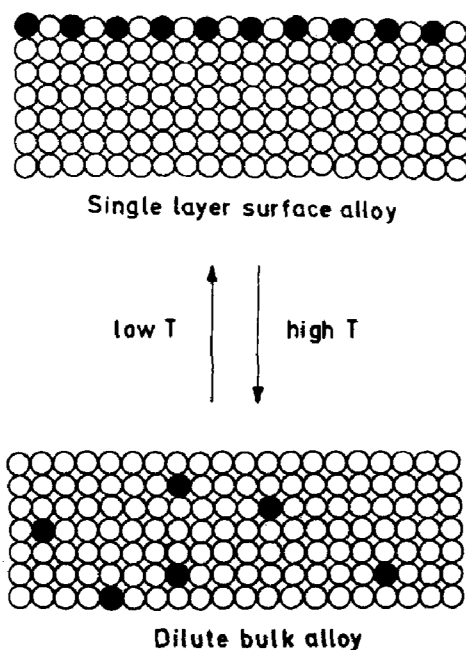
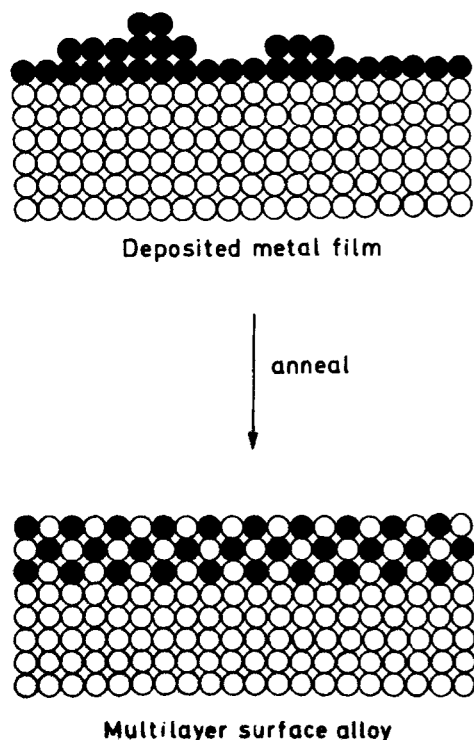


Figure 8. Bulk-surface phase equilibria at the surface of alloys. From ref. 19.

## Faceting of metal surfaces

Faceting is a surface phenomenon observed on transition metal surfaces such as Pt(100), Pt(110), and W(111). It can expose crystal planes of different orientations containing monoatomic steps. A well-defined metal surface can also undergo faceting when a metal vapour is deposited at a certain temperature. Faceted surfaces can significantly influence the activation energies, product distribution and reaction rates. It has also been reported that kinetic oscillations of reactions on single crystal surfaces are often associated with the faceting phenomenon<sup>46</sup>. The rate of oxidation of CO to CO<sub>2</sub> on Pt(110) is tremendously influenced by faceting which exposes periodic arrays of steps and terraces corresponding to (430) and (210) orientations. Moreover, certain transition and noble metals deposited on the W(111) and Mo(111) substrates can induce striking morphological instabilities on the substrate<sup>47</sup>. The substrate restructures to form microscopic 3-sided (4-sided on Rh(001)) pyramids with facets oriented in (211) directions upon annealing at elevated temperatures<sup>48,49</sup>. This phenomenon is referred to as faceting (Figure 12).

The (211) orientation of pyramidal facets is detected by LEED and confirmed by real space images obtained using STM. Several investigations indicate that there is a critical coverage needed to induce surface reconstruction of W(111). For a Pd/W(111) system, the critical coverage is one 'physical monolayer'. The number of overlayer atoms that are needed to cover all of the exposed W

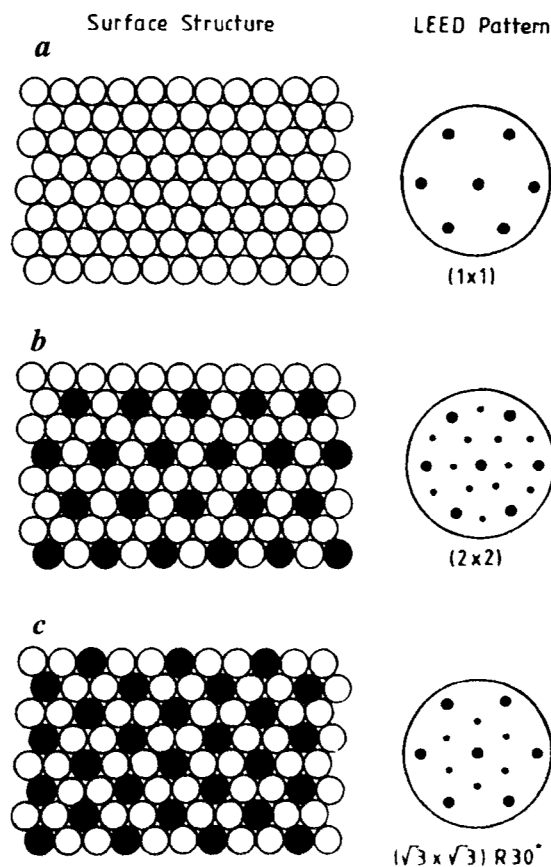


**Figure 9.** Schematic illustration of the mechanism of formation of multilayer surface alloys by diffusion process. From ref. 19.

atoms is defined as a 'physical monolayer', and corresponds to an atomic density of  $1.71 \times 10^{15}$  atoms cm<sup>2</sup>. It is important to note that faceting of W(111) is not induced by all ultrathin overlayer films. The driving force for faceting could be the tendency for a system to achieve the minimum total surface free energy. It is necessary to explore the reasons for faceting which may further help in understanding the metal-metal bonding and interface interactions. There may be a correlation between the properties of the overlayer and the faceting phenomenon. The factors such as atomic size, Pauling electronegativity ( $> 2.0$ ) are some of the useful parameters in characterizing the energetics and morphological stability of bimetallic interfaces<sup>47</sup>. Investigations on faceting, alloy formation in faceting and the associated oscillatory nature of surface chemical reactions are rapidly expanding at present.

## Surface chemistry and catalysis

There are a number of alloy systems reported in literature<sup>2,5,50</sup>. These reported studies are essentially related to the evaluation of structural, electronic, chemical, and catalytic properties of bimetallic surfaces. The most important alloys that are often used in catalyst formu-



**Figure 10.** The schematic view of surface structures and their LEED pattern observed during the deposition of Sn on Pt(111) surface: (a) clean Pt(111), (b) (2x2) alloy structure and (c) ( $\sqrt{3} \times \sqrt{3}$ ) R30° alloy structure. From ref. 42.



lations are; Pt alloys, and Pd alloys. These alloys often show better catalytic activity and selectivity (Table 1) compared to their pure constituents<sup>1-5,28,51</sup>, and are often investigated using well defined crystals<sup>16-18,34,52</sup>. For industrial purposes, Pt-metal or Pd-metal alloys are used as small particles deposited on a substrate, and catalytic reactions for these alloy phases have been studied<sup>28,53</sup>. The supported catalyst is the one most difficult to study because of its complexity, and therefore recourse is often made to simpler systems, like particular faces of single crystals or model catalysts fabricated in a more controlled way<sup>54</sup>. In order to fully understand the catalytic potential of a bimetallic system, one needs to perform surface science investigations to collect atomic level information on structure, composition, adsorption and desorption, surface chemical bonding, and catalytic activity and selectivity. This approach helps us to envisage the surface dynamics and molecular transformation pathways on the surface sites. It has been applied quite successfully to metal catalysts<sup>55</sup> and more recently to bimetallic surfaces<sup>2,3,17,50</sup> as well.

We shall discuss the example of Pt-Rh alloys. Pt-Rh gauzes are used for the production of nitric acid which is used in the manufacture of nitrate fertilizers. Another major application of Pt and Rh is in TWCs. TWC is the so-called three-way catalyst used for the treatment of the two reducing pollutants, namely, carbon monoxide and uncombusted hydrocarbons, and the oxidizing pollutant, namely, oxides of nitrogen present in the automobile exhaust emissions. The noble metals are

found to be in the form of bimetallic particles in TWC. This is the reason why much of the fundamental research has been devoted to the characterization of the Pt-Rh alloy surfaces, and to the effect of alloy formation on the chemical properties<sup>3,28,56</sup>. The catalytic work on supported Rh and Pt metals has also been pursued to throw light on some related aspects<sup>57,58</sup>.

One of the important observations noted in all these fundamental studies is that NO dissociates easily on Rh. Bond breaking in NO is considered as the first step in the reduction of NO by CO and hydrogen. By contrast, Pt and Pd metals are less able to dissociate NO than Rh metal. Therefore, NO chemisorption is a sensitive probe for examining the possible effect of alloy formation. It is observed that the Rh atoms on the alloy surface are very effective in the NO dissociation, that is it occurs mainly on Rh sites. The mixed Pt-Rh sites are not very active in NO bond breaking. These results show that the formation of Pt-Rh alloy particles in the TWC is undesirable. Alloy particles, when they exist would also tend to develop Rh-rich surface under operating conditions. In any case, results on Pt-Rh surfaces demonstrate that alloys with uniform, intermediate surface composition exhibit behaviour which is intermediate to that of their constituent metals. The characteristics which distinguish Rh are thus less pronounced in Pt-Rh alloys.

Further, we shall consider the chemisorption properties of Pt and Pd alloy surfaces, and present only the general aspects of this subject. For chemisorption, it is necessary to consider the factors that determine the adsorption bond strength on pure metals. The heat of adsorption is basically a culmination of several contributions: (i) Sensitivity of the heat of adsorption to the surface and electronic structure of the metals, and (ii) effect of both attractive and repulsive lateral interactions within the adlayer of molecules.

The heats of adsorption of CO and N<sub>2</sub> are different for different metals. This is related to the electronic structure of a metal as well as dependent on the surface structure. For example, Fe(111) face is highly active for ammonia synthesis. This is attributed to the presence of Fe atoms with a coordination number of 7 (C<sub>7</sub> sites). Therefore, the heat of adsorption depends on the coordination number of a particular site and one can expect a number of different sites on a single plane. The lateral interactions between the molecules may lead to the

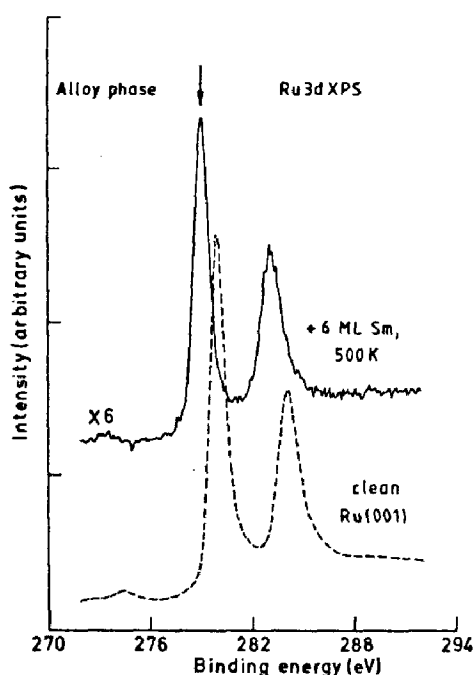


Figure 11. The Ru 3d XPS spectra of clean Ru(001) surface and SmRu intermetallic alloy phase formed on Ru(001) surface. From ref. 44.

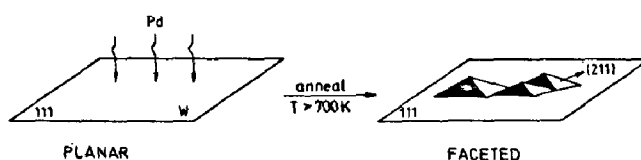


Figure 12. A schematic drawing of faceting of W(111) surface induced by ultrathin Pd films. From ref. 49.



formation of ordered molecular domains. In the case of adsorbed CO and H<sub>2</sub> on metals, the heat of adsorption decreases with increasing coverage. This is caused by the occupation of less favorable sites (geometric) and the lateral interactions (repulsive) in the compressed adlayer. When a metal is alloyed with another, many others factors are to be considered in understanding the adsorption behaviour. The variations in adsorption properties observed upon alloying a metal X with another metal Y have been attributed to: (i) ensemble or geometric effect in order to explain differences in surface reactivity upon alloying, (ii) changes that occur in the electronic structure of metal X as a result of the addition of metal Y (ligand effect), and (iii) the surface structure of an alloy phase, as in metals.

In general, the following effects of alloy formation have been observed in most of the ordered bimetallic crystal surfaces with the exception of Pt–Rh. There is; (i) a decrease in the CO and hydrogen uptake, (ii) a change in the relative population of the various adsorption states, (iii) a shift in desorption temperature to lower values, and (iv) a lowering of the activity in bond breaking of the adsorbed molecules.

The smaller heat of adsorption, when a metal X is alloyed with a metal Y, can be partly understood in terms of dilution effects resulting in reduced lateral interaction and increased occupancy of less favourable sites. However, for CO, the shifting of desorption temperatures to lower values at low exposures, as a result of alloying, is ascribed to a ligand effect. For Pd-based alloys, the estimated energy changes for lateral interactions and ligand effects are of the order of 15 kJ/mol and 10 kJ/mol, respectively<sup>3</sup>.

It has been suggested that dissociation of the hydrogen molecule requires a cluster of several adjacent metal X atoms. However, there is experimental evidence for hydrogen dissociation on isolated Pd atoms as well. Therefore, the lower uptake of hydrogen can be the result of a lower heat of adsorption. The heat of adsorption is much lower on isolated Pd atoms or singlet Pd sites than on triplet Pd sites.

In case of Pt alloys, the decrease in heat of adsorption is explained as Pt–Pt bond contraction, and the strong Pt–X bond between the top two layers. These factors are responsible for the low activity of Pt alloys in chemisorption and bond breaking.

## Summary

This article briefly introduces the topic of 'Chemistry of Bimetallic Surfaces' in a qualitative manner. We have highlighted the current aspects in this area and discussed them in detail wherever possible with suitable examples and references. The phenomena of segregation, faceting, and surface chemical oscillations have been drawing more attention for further research. In catalysis, it is

easy to imagine that, besides the presence of various kinds of surface sites, the aggregates and polycrystalline samples will develop facets exposing various low index faces to surface reactions. However, it is not clear whether surface alloying and faceting are synergetic to each other. It is evident that the motivation behind the study of chemistry of bimetallic systems is to understand their superior activity and selectivity. Also certain chemical reactions that may not even occur on pure metal system, can be achieved on alloys. In future, more number of bimetallic systems will be employed as catalysts in automotive exhaust catalysis, hydrocarbon synthesis, hydrocracking in oil industry and so on. Therefore, the study of bimetallic surfaces and particles has become an important field in surface chemistry and catalysis. It should be mentioned that ternary systems have not been explored systematically yet. The available database on physical and chemical aspects the bimetallic systems so far and the future investigations focusing on alloy surfaces at an atomic scale will certainly help us more in understanding the surface structure, reactivity, chemisorption, heterogeneous catalysis, and other related phenomena which may occur on bimetallic surfaces.

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ACKNOWLEDGEMENTS. I thank Dr K. Mangala Sunder Krishnan and my student H. R. Sahu for their help. The CSIR, New Delhi, is acknowledged for financial support.

Received 13 March 1998; revised accepted 21 August 1998