

Defects on surfaces

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Abstract. A brief review of various types of defects on surfaces and their role in surface reactions is presented. Particular emphasis is given on defects like steps/kinks and additives (promoters and poison)

Keywords. Defects; surfaces; steps; kinks; additives.

1. Introduction

The importance of defects on surfaces has long been recognized in surface reactions and in recent years several careful studies on surfaces with impurities or structural defects have shown that such surfaces have significantly different reaction rates as compared to (almost) defect-free surfaces (see Somorjai 1984). Another area where defects have played a central role is the studies on crystal growth (see Gilmer 1984 and references therein). Most common defects on even the ideally prepared single crystal surfaces are vacancies, adatoms, steps, kinks and impurities (substitutional, interstitial or adatom). These are illustrated in figure 1. In addition islands (particularly for overlayers), dislocations, phase boundaries and in the case of polycrystalline materials grain boundaries may be present. The lower coordination at a surface itself sometimes leads to significant structural modifications. Because of the absence of half the crystal, the electronic charge density distribution at a surface is different from its value in the bulk and the ions in the vicinity of the surface adjust to new equilibrium positions consistent with this new charge density. This leads to relaxation of surface ions from their bulk positions. This relaxation is large for relatively open surfaces and has in-depth oscillatory behaviour (see Barnett *et al* 1983 and references therein). For high Miller index surfaces like Fe (310) horizontal relaxation has also been observed (Sokolov *et al* 1984). In such cases the surface has the tendency to become more closely packed. Surfaces with chemisorbed species tend to recover their bulk positions and sometimes there is also an outward relaxation of the topmost layer as in the case of oxygen on Ni (100) surface (Frenken *et al* 1983). These relaxations can play an important role in surface compound formation such as oxidation etc. More important is the reconstruction of relatively open surfaces like the (1×2) reconstruction of the (110) surface of Ir, Pt and Au or (7×7) reconstruction of Si (111) surface etc (see Estrup 1984). In some other cases where the clean surface is stable, reconstruction may occur under surface reactions. Understanding these structural changes has been a difficult task. In recent years it has become possible to directly see the surface atomic structure with the development of the scanning tunnelling microscopy (STM) (Binnig *et al* 1982). This new tool has vastly improved our knowledge of surface structure and defects. It is also becoming possible to monitor surface structure modifications under reactions (Hosler *et al* 1986). In this brief review some of these recent developments and the physical understanding of the role of defects in surface reactions are discussed. Temperature

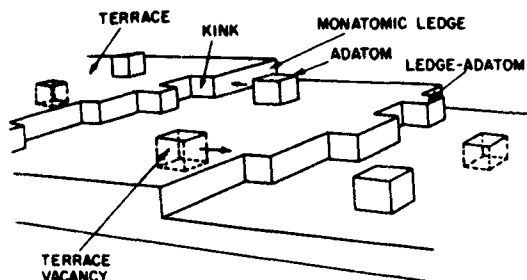


Figure 1. Illustration of some of the defects at a free surface.

plays an important role in surface reactions and it can also change the defect concentration. Sometimes at low temperatures there is a reversible reconstruction of the surface as for the (100) surface of Mo and W (Estrup 1984). For alloys surface chemical concentration is in general different from its bulk value (Kumar 1981; Kelley and Ponc 1981 and references therein) and there can be order-disorder transitions as the temperature is varied (Kumar and Bennemann 1984). Also at higher temperatures surface roughening may take place (Leamy *et al* 1975) but all these topics will not be covered here.

2. Techniques to detect defects

Point defects like vacancies and impurities are in general difficult to detect. If the impurity concentration is $\geq 1\%$ of a monolayer, it can be detected by Auger electron spectroscopy (AES). Surface relaxations have been measured using ion scattering spectroscopy (ISS) (Frenken *et al* 1983) and by low energy electron diffraction (LEED) intensity analysis (Noonan and Davis 1984). Surface reconstruction, steps, kinks (for e.g. on a high Miller index surface), order-disorder transitions etc are easily observed in a diffraction experiment like LEED (Lagally 1982; Wagner 1979), He diffraction (Engel and Rieder 1982; Poelsema *et al* 1983) etc. Field ion microscopy (FIM) is one of the important tools to determine surface structure, but this technique is limited to those materials for which a fine tip can be prepared (Tsong 1986 and references therein). All these techniques (except for FIM) and other surface sensitive techniques like SEXAFS, XANES, photoelectron diffraction, electron energy loss spectroscopy etc (see Rieder 1986) provide valuable information about the surface structure on an average and a detailed discussion of these is not given here. The determination of the atomic structure in the case of (say) reconstruction, structural disorder and defects is in general difficult. It is only in recent years with the development of the STM that quantitative structural analysis has become possible. In the following some of the results obtained with this technique are presented.

The physical basis of the STM is electron tunnelling between two conductors separated by a thin insulating layer (generally vacuum) that constitutes the potential barrier. As the tunnelling current depends upon the overlap of the wavefunctions in the insulating region, it strongly depends upon the separation of the two electrodes and also the type of electronic states involved. In practice a fine metal tip* usually

*These days it is possible to prepare tips with a single atom using FIM technique (Fink 1986).

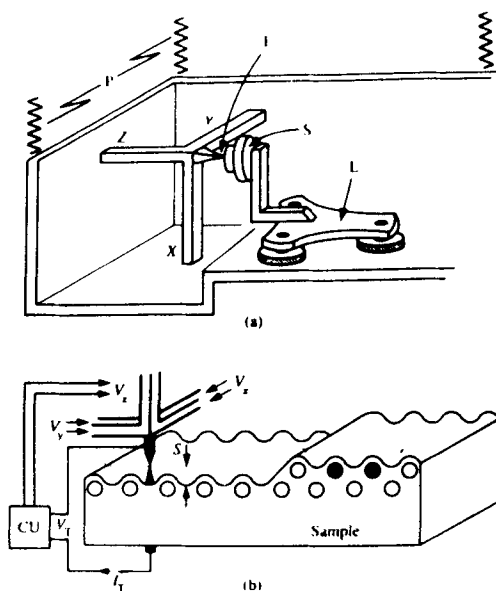


Figure 2. Schematic of a scanning tunneling microscope and its operation. The tip T of the microscope depicted in (a) is scanned over the surface of a sample S with a piezoelectric tripod (X, Y, Z). The rough positioner L brings the sample within reach of the tripod. A vibrational filter P protects the instrument from external vibrations. In the constant tunnelling current mode of operation, a voltage V_z is applied to the Z piezoelectric element by means of the control unit CU depicted in (b) to keep the tunnelling current constant while the tip is scanned across the surface by altering V_x and V_y . The trace of the tip resembles the surface topography (after Binnig and Rohrer 1986).

prepared from tungsten wire is scanned over the surface of a sample (figure 2). In the constant current mode with a certain applied voltage, say v_z in the z direction, the tip is moved up and down as it scans the surface in the x-y plane. The tip movement generally resembles the surface topography. One such scan is shown in figure 3 for the Au (100) surface. This shows flat terraces and also monolayer step lines. The wavy structure represents individual atomic rows. This study clearly showed that even for almost ideal surfaces, steps are a common feature. Another early important application of the STM in which its potential was clearly demonstrated was the determination of the atomic structure of the reconstructed (110) surface of Ir, Pt and Au. The (110) surface has compact rows along the (110) direction and along the (001) direction the periodicity is doubled for the reconstructed surfaces. The complexity of the structural determination is clearly revealed from the fact that before STM there have been several models to explain it. These included (i) pairing of rows, (ii) buckled surface, (iii) missing row, (iv) missing row combined with pairing in the second layer and (v) saw tooth structure. All these are shown in figure 4. Though on the basis of the LEED intensity analysis, the preferred model has been a missing row model but the agreement between the model and the experiment has been only marginally satisfactory (see Adams *et al* 1981). It is only after the STM was developed that pictures with atomic resolution could be obtained (Binnig and Rohrer 1983) which showed (figure 5) not only (1×2) reconstruction for the Au (110) surface but also (1×3) and (1×4) which were not seen in LEED. Also the surface

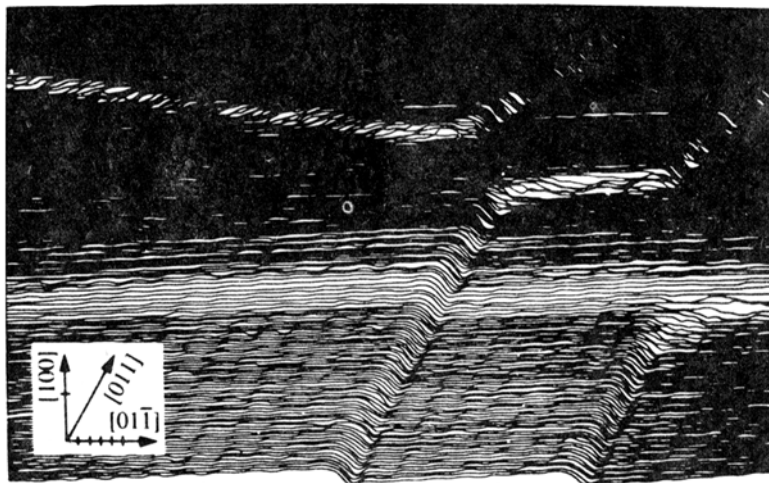


Figure 3. STM image of a clean Au(100) surface obtained at a constant tunnelling current of 1 nA, showing flat terraces and monolayer step lines. The wavy structure is real and can be resolved into individual atomic rows. The division of the axes corresponds to spacings of 5 \AA (after Binnig *et al* 1984).

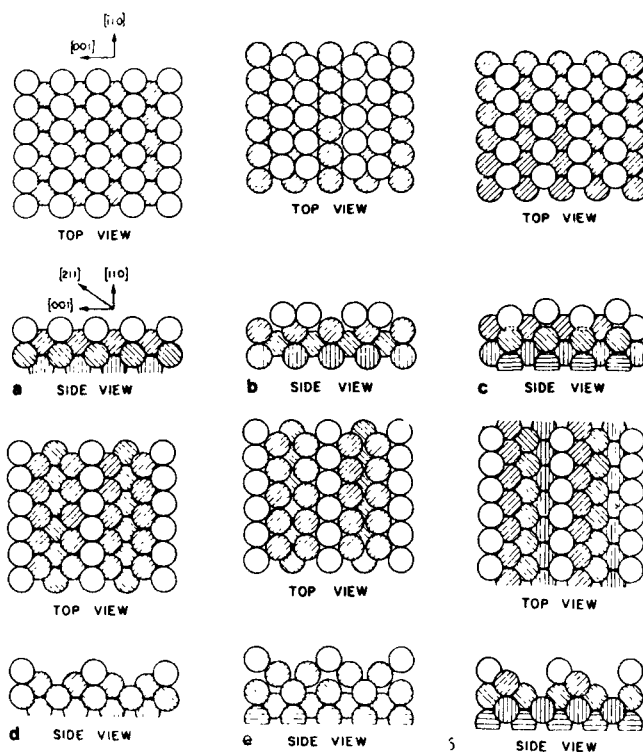


Figure 4. (a) Unreconstructed fcc(110) surface. Open circles represent the top layer atoms and the shaded circles represent the second, third and fourth layers. Other figures show different models of (1×2) reconstruction. (b) Paired row model. (c) Buckled surface model. (d) Missing row model. (e) Missing row combined with pairing of the second layer and (f) saw tooth model (from Estrup 1984).

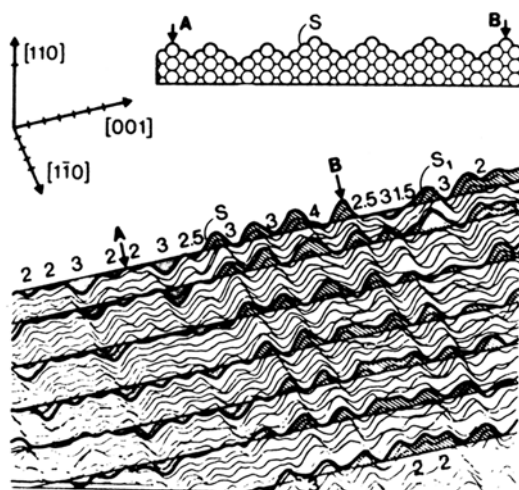


Figure 5. STM picture of a (1×2) reconstructed Au(110) surface. It consists of narrow (111) facets along the (110) direction. Divisions on the crystal axes are 5 \AA . The straight lines are drawn to help visualization of the structure. Below each line the missing rows and above each line the remaining rows are shaded. The numbers on the top scan show the distance between maxima in units of the bulk lattice constant. The inset shows the proposed structural model for the observed corrugation between A and B. It shows not only (1×2) reconstruction but also (1×3) and (1×4) . There is also some disorder present at the surface (after Binnig and Rohrer 1983).

showed a lot of disorder. After these early developments in the IBM Zurich Laboratory, STM has been developed and used in several other laboratories (mostly in the west) to study a variety of surfaces of metals, semiconductors etc and better resolutions have been obtained since then. The reader can get a good account of these in articles published in July and September 1986 issues of the IBM Journal of Research and Development. The applications of the STM for surface and interfacial atomic structure determination are immense and what we have seen is just the beginning. For surface chemical reactions it is important to understand which sites are the most active and what happens to a surface after a reaction has taken place. This has been done recently (Hosler *et al* 1986) where the study of the structure before and after the decomposition of ethylene on Pt(100) surface has led to the conclusion that the steps are the active sites and that under the reaction the surface becomes rough (figure 6). The same group has also used the STM to monitor the temperature-dependent defect structure of a Pt surface.

3. Reactivity of surfaces with defects

For surface reactions the surface atomic structure plays a very important role. That is why different surfaces of the same material show different reactivities. A well-known example is the ammonia synthesis in which Fe is used as a catalyst. It has been found that the (111) surface of iron is 420 times more active and the (100) surface is 32 times more active than the closed packed (110) surface (Spencer *et al* 1982). Presence of steps and kinks modifies the reaction rate further. Flat Pt surfaces

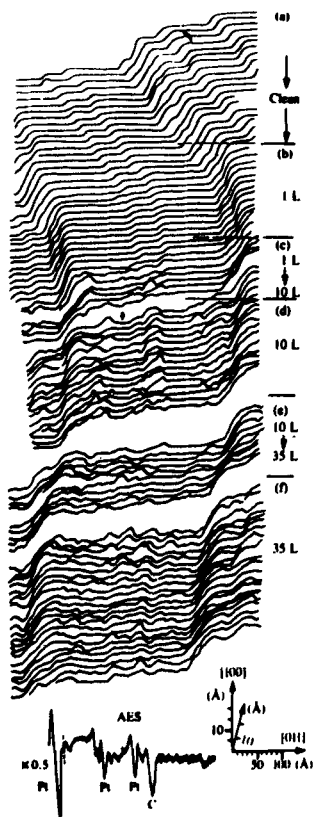


Figure 6. Decomposition of ethylene on Pt(100) surface at 550 K. (a) Two-dimensional STM scans of the clean surface which shows terraces and steps. (b)-(f) Two-dimensional scans of the surface after increasing amount of exposure of ethylene. The terraces are seen to become rough as the ethylene exposure is increased. The Auger spectrum indicates the presence of graphite on the surface (after Hosler *et al* 1986).

do not dissociate CO but stepped surfaces do. Similarly H_2 dissociation on Pt (111) surface is activated but with stepped surfaces dissociation takes place without the activation barrier. Furthermore in several industrial applications involving organic molecules, we deal with breaking of C-H or C-C bond. Modifying the surface structure facilitates the selectivity of reactions as one of these bond breaking may become more preferred. The question then arises: what role do steps and kinks play and where exactly does a reaction take place? To answer these questions detailed experiments have been performed during the last few years under controlled conditions. To understand the role of steps and kinks experiments have been done on high Miller index surfaces (Somorjai 1984) while for impurities coadsorption experiments have been done (Ertl *et al* 1982; Goodman and Houston 1987; Kiskinova and Goodman 1981). In the following we describe the two separately.

3.1 Steps and kinks

In an industrial catalyst step and kink density can be quite high. In the laboratory high density of steps and kinks can be obtained by cutting low Miller index

orientation single crystals at some angle w.r.t. the low index orientation. These high Miller index surfaces exhibit ordered terraces separated by periodic steps. The step periodicity and the step height can be determined by LEED experiments (see Blakely and Eizenberg 1981). High Miller index surfaces can be cut such that they have 40% of their atoms in step sites and kink concentration can reach 10%. These concentrations of line defects are much higher than point defects usually present on surfaces. Also steps and kinks are often stable under conditions of catalytic reaction. In figure 7 we show the HD production rate when a mixture of H_2/D_2 is incident over the Pt(332) (which has steps) and Pt(111) (which is closed packed) surfaces (Somorjai 1984). As the angle of incidence of the mixed molecular beam is varied, HD production rate shows a sharp variation. When the beam is incident normal to the step, the reactivity is maximum. Also overall as compared to the Pt(111) surface, the reactivity of the high Miller index surface is more than three times higher. This study clearly shows that molecules get preferentially dissociated at the step sites. Similar preferential C-H or C-C bond breaking has been seen for organic molecules on steps and kinks. Dehydrogenation of cyclohexane to benzene is seen to be independent of

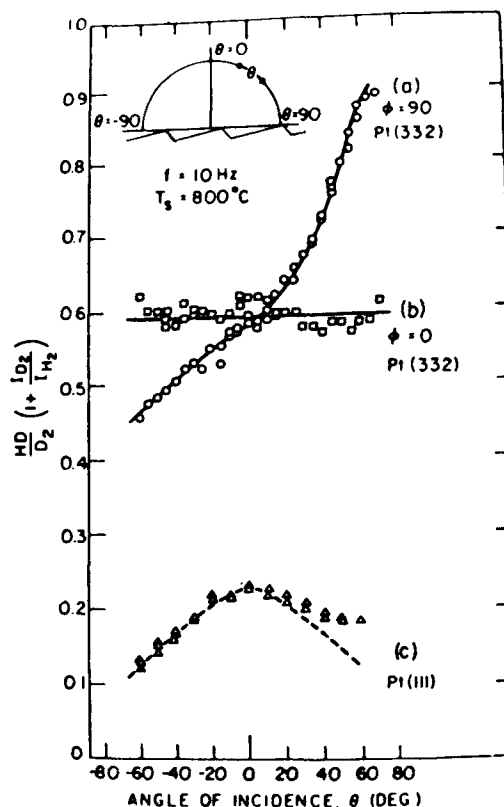


Figure 7. HD production during H_2/D_2 dissociation as a function of angle of incidence of the molecular beams. Intensity of the HD molecules is normalized to the incident D_2 intensity. (a) Pt(332) surface with stepped edges perpendicular to the incident beam ($\phi = 90^\circ$) shows the highest reactivity. (b) Pt(332) surface where the beam is incident parallel to the step edges. $\phi = 0^\circ$ and (c) Pt(111) surface exhibit almost an order of magnitude lower reactivity (after Somorjai 1984).

step density at 125°C while the hydrogenolysis to *n*-hexane increases almost linearly with step density. The same is true with kinks but the rate of hydrogenolysis is higher (by an order of magnitude) in the case of kinks (Somorjai 1984). So kinks seem to be more effective for breaking C-C bond in addition to breaking C-H and H-H bonds while steps are active for C-H bond breaking but not so for C-C bond breaking. This selectivity of atomic structure in bond breaking is significant as the atomic structure of a catalyst can be tailored to provide selectivity in chemical reactions where C-C and C-H bond breaking processes are to be separated. A similar effect can be obtained by putting additives on the surface.

3.2 Additives

We can distinguish two types of additives which can effect the performance of a catalyst. (i) Those which are intentionally added to the surface during catalyst preparation like promoters (Na, K, Cs etc.) or poison (Cl, O, P, S, etc.). Also in some cases other metals can be used to block certain sites (for e.g. Au on Pt or Ir surfaces). Similar effects can be obtained by alloying as for Cu-Ni alloys or other bimetallic clusters (Sinfelt 1986). Sometimes additives are also used to stabilize the surface structure or oxidation state which could otherwise be unstable when the reaction proceeds. (ii) Those which are in the reaction mixture and get deposited on the surface like carbonaceous layer or oxide deposits. Much work has been done to understand the role of these two. It has been found (Ertl *et al* 1982; Campbell and Goodman 1982) that for dissociation of H₂, CO, NO, N₂ etc. presence of a few percent of electropositive elements like Na, K, Cs etc enhances the binding energy of the molecule and the probability of dissociation increases as compared to desorption. Whereas electronegative elements like S, O, Cl, P etc reduce the binding energy of the molecule as observed from thermal desorption spectroscopy (TDS) (Kiskinova and Goodman 1981) and hence the desorption probability increases as compared to dissociation. These two types of additives thus effectively increase or decrease the reaction rate. This is shown in figure 8 for CO dissociation. In other cases like NH₃ or H₂O, the role of electropositive and electronegative additives is reversed.

In general additives can have two effects: (i) The electrostatic effect which changes the electronic structure and the work function of the surface. This will be discussed in the next section. (ii) The additives may preferentially sit on the active sites thus effecting surface reaction. This is very common for additives which are produced under the surface reactions. As discussed previously, when a reaction proceeds on a step or kink site, carbonaceous species or graphitic carbon get preferentially deposited on such step sites inhibiting the reaction. Even for flat surfaces if the dissociation of a molecule requires a certain minimum number of sites then the presence of additives can block some of these sites and effect the surface reaction. Additives may also change the surface structure which may either increase or decrease the reactivity.

4. Electronic effects

We have seen that steps/kinks and electropositive additives tend to increase the reaction rate for molecules like NO, CO, H₂, N₂ etc. To understand this it is first to be noted that surfaces with these defects have lower work function (see Kiejna and

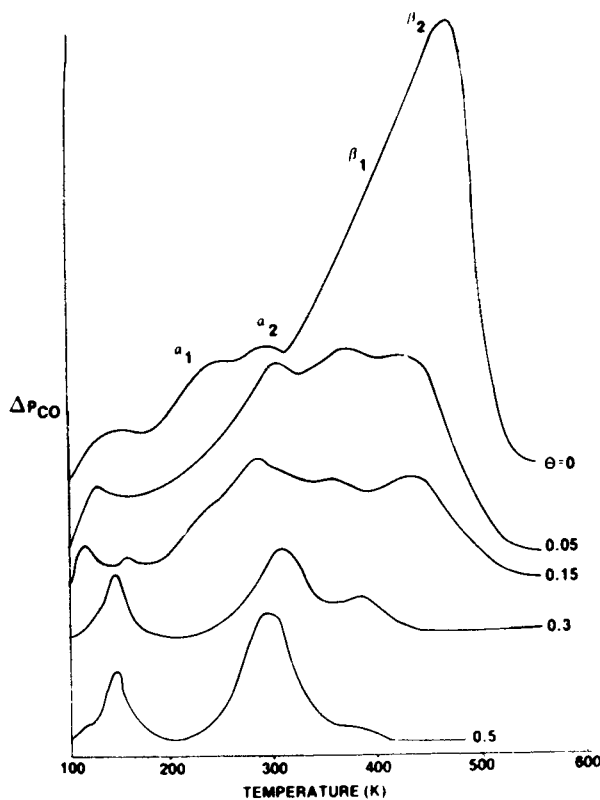


Figure 8. Thermal desorption spectra of molecular CO adsorption on Ni(100) surface in the presence of various amounts of sulphur. It is seen that the presence of only 5% of S reduces the intensity of the peak drastically (after Kiskinova and Goodman 1981).

Wojcichowski 1981). For stepped surfaces there is a smoothing of the electronic charge density which creates a dipole opposite to that for a flat surface. This reduces the work function (Smoluchowski 1941). Similarly electropositive (electronegative) adsorbates give rise to decrease (increase) in the work function. This measured decrease (increase) in the work function represents an average over the whole surface. It is, however, instructive to consider the changes in the local work function which reflects the change in the local electrostatic potential with respect to the Fermi energy. Since the dissociation of a molecule requires transfer of electrons to the antibonding levels, it can be achieved more efficiently in the vicinity of the sites having a lower work function and that is why steps/kinks or electropositive additives increase reactivity. This appealing explanation, however, does not explain why even less than 10% additives change the reactivity by orders of magnitude and how does additives influence the binding energy of the molecules. Nørskov *et al* (1984) have calculated the change in the binding energy of a molecule in the presence of an adsorbate using the effective medium theory. In this approach it is assumed that the distance between the coadsorbed species is large enough to allow the effect of one on another adsorbed species to be treated in a perturbative way. Thus in the lowest order the effective one electron potential inside the region 'a' containing the molecule is treated to be independent of the changes in the host outside this region and outside

this region the potential is treated to be independent of the changes due to the presence of the molecule. This approximation enabled Nørskov *et al* (1984) to write the change in the binding energy δE_B of a molecule in the host which is changed due to the presence of coadsorbates (here promoter or poison) in the local density functional approach as

$$\delta E_B = \int_a \delta\phi_0(\mathbf{r}) \Delta\rho(\mathbf{r}) d\mathbf{r} + \delta \left[\int_{-\infty}^{E_f} \Delta n(e) e de \right], \quad (1)$$

where $\delta\phi_0(\mathbf{r})$ is the change in the electrostatic potential at the surface due to the coadsorbate and $\Delta\rho(\mathbf{r})$ is the induced charge density due to the molecule. $\Delta n(e)$ is the change in the one-electron density of states when the molecule is embedded in the host (with the coadsorbate). The first term represents the electrostatic interaction between the molecule and the coadsorbate while the second term includes changes in the one-electron energy. The contribution of the second term is small in most cases of interest as the direct overlap between the molecule and the coadsorbate is usually small and it is mainly due to indirect interactions whose magnitude is of the order of 10 meV. Therefore neglecting this contribution δE_B can be calculated with a knowledge of $\delta\phi_0(\mathbf{r})$ which has been calculated by Lang and Williams (1982) for a number of atoms outside a jellium surface (figure 9) and $\Delta\rho(\mathbf{r})$ due to the molecule. The latter term is difficult to calculate. It is seen from figure 9 that $\delta\phi_0(\mathbf{r})$ is small inside the metal surface (here the jellium edge) and so only $\Delta\rho_a(\mathbf{r}_a)$ of $\Delta\rho$ (in the vicinity of the molecule) contributes significantly to equation (1). Defining $\delta\phi_0$ as

$$\overline{\delta\phi_0} \int_a \Delta\rho_a(\mathbf{r}) d\mathbf{r} = \int_a \delta\phi_0(\mathbf{r}) \Delta\rho_a(\mathbf{r}) d\mathbf{r}, \quad (2)$$

$$\delta E_B = \overline{\delta\phi_0} Z_a. \quad (3)$$

where

$$Z_a = \int \Delta\rho_a(\mathbf{r}) d\mathbf{r} \quad (4)$$

measures the charge transfer from or to the molecule. For dissociation of the

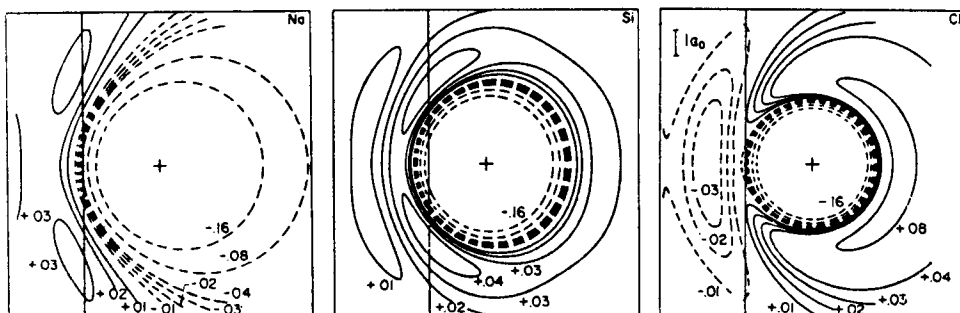


Figure 9. Equi-potential contours of the atom induced electrostatic potential for Na, Si and Cl chemisorbed on an $r_s=2$ jellium surface, shown in a plane perpendicular to the surface through the atomic nucleus which is shown by a cross. The jellium edge is indicated by a vertical line. Contours of positive (negative) induced potential are shown by full (broken) lines in units of Ry. (after Nørskov *et al* 1984).

molecule antibonding level gets partly occupied and so (3) gives the energy change when the antibonding level of the molecule is shifted by $\delta\bar{\phi}_0$ or the local work function is changed by $\bar{\delta\phi}_0$. Since Z_a is positive, the sign of ΔE_B is given by $\bar{\delta\phi}_0$. Taking $\bar{\delta\phi}_0 \approx \delta\phi(\mathbf{r}_a)$ with \mathbf{r}_a the centre of the adsorbed atom, from figure 9 $\delta\phi_0(\mathbf{r}_a)$ is negative (positive) for electropositive (electronegative) adsorbates. Correspondingly the molecular binding energy increases (decreases) as it was concluded from experiments (§ 3). This increase (decrease) in the binding energy will result in the decrease (increase) in the activation barrier for the dissociation of the molecule thereby enhancing (decreasing) the reaction rate.

The electrostatic potential shown in figure 9 falls off to 0.01 Ry within roughly $6a_0 \approx 3 \text{ \AA}$ ($a_0 = \text{Bohr radius}$) parallel to the surface and so the nearest neighbours are strongly affected due to promoters and poison and the effect is small beyond second neighbours. This range also depends upon the size of the adsorbates. For Cs this effect is more pronounced as compared to Na. It is due to the fact that screening outside the metal surface becomes less effective.

The effect of promoters and poison on the adsorbates like NH_3 can also be understood in this model. These molecules have a large dipole moment. When NH_3 is adsorbed on Fe surface with N pointing towards the surface, there is a large decrease of the work function (Grunze *et al* 1978). This means that the electronic charge is transferred far away from the surface where the potential due to electropositive additives is negative and large, towards the metal surface where the screening is more effective. This would lead to lower binding energy according to the arguments presented above and hence electropositive adsorbates will act as poison for NH_3 and electronegative adsorbates as promoters.

Feibelman and Hamman (1984, 1985) discussed the importance of the density of states at the Fermi energy. They have done a calculation of the electronic structure of sulphur on Rh(001) surface using the linearized augmented plane wave (LAPW) method for 1/3 and 1/4 monolayer coverages. They found that though the charge transfer due to the adsorbate is screened out very efficiently, changes in the local density of states (LDOS) at the Fermi energy (E_F) prevail over longer distances. Electropositive (electronegative) elements have the effect of increasing (decreasing) the LDOS at the E_F . An increase (decrease) in the LDOS at the E_F facilitates (inhibits) charge transfer to antibonding molecular levels and thus effects the dissociation of the molecule.

5. Conclusions

In summary we have discussed various types of defects which are commonly present on a surface and have given examples of the role played by steps and kinks and additives on some surface reactions. From an industrial point of view it is an important problem and we are beginning to understand the physical basis of promoters and poison and other defects. This will no doubt help us in preparing better catalysts. Moreover such studies will prove helpful in understanding other surface reactions like corrosion and interfacial phenomena like embrittlement. Applications of the scanning tunnelling microscope would be a major area of research in the near future and we hope that such studies will provide answers to several problems of not only the gas-solid surface interaction but also liquid-solid interfaces, electrochemistry, biological systems etc.

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