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TOPICAL REVIEW

Adsorption and dissociation of benzene on bimetallic surfaces—the influence of surface geometry and electronic structure

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Abstract

This topical review discusses the influence of the surface geometry (e.g. lattice parameters and termination) and electronic structure of well-defined bimetallic surfaces on the adsorption and dissociation of benzene. The available data can be divided into two categories with combinations of non-transition metals and transition metals on the one side and combinations of two transition metals on the other. The main effect of non-transition metals in surface alloys is site blocking which can suppress chemisorption and dissociation of the molecules completely. When two transition metals are combined, the effects are less dramatic. They mainly affect the strength of the chemisorption bond and the degree of dissociation due to electronic and template effects.

Contents

1. Introduction

Bimetallic surfaces play an important role in heterogeneous catalysis, electrochemistry and metallurgy, and have therefore attracted increasing interest among surface scientists over the past two decades (for recent reviews see [1–6]). Through the combination of different metals the surface geometries and electronic structures can be varied and, as a consequence, the reactivities of these surfaces change. This is used to optimize industrial catalysts for a wide range of applications. Examples are petrol reforming or the purification of automotive exhaust gas, in which cases the active catalyst materials usually consist of Pt in combination with another metal such as Re, Rh, Ir, Au or Sn. For a general understanding of trends in the physical and chemical properties of this class of materials, systematic studies of bimetallic surfaces with many different constituents are necessary. Points of fundamental interest are the nature of heteronuclear metal–metal bonds and the elementary steps of surface reactions, such as the adsorption and dissociation of molecules. Some trends in the surface chemistry of small molecules, e.g. CO, NO and N_2, are already well understood due to extensive recent theoretical studies in this field (see, e.g., [7–11]). However, such detailed understanding has not yet been achieved for larger organic molecules on bimetallic surfaces. Benzene is the best studied example, representing a class of aromatic molecules which play an important role in petrol reforming and many other catalytic processes.

In contrast to the small molecules mentioned before, which form a bond to the metal surface only through one of their atoms, the benzene–surface bond usually involves the entire C_6 ring. Therefore, the match between the adsorption sites provided by the surface and the shape of the molecule with respect to the atomic positions and the electronic charge distribution is much more critical. This leads to a number of interesting new effects in the surface chemistry of benzene on bimetallic surfaces, which is the subject of this review. In the following sections we review the information available to date on the adsorption and dissociation of benzene on well-defined bimetallic surfaces. With benzene being one of the model organic molecules for surface science, a large amount of data regarding the adsorption on monometallic single-crystal surfaces is at hand [12] for comparison. Although the number of studies involving bimetallic systems is still relatively small compared to this database, there are already enough results to identify certain trends which may serve as a motivation for further investigations.

1.1. Adsorption and reactivity on bimetallic surfaces

The largest bimetallic effects on the reactivity can be expected when each surface metal atom has at least one nearest neighbour of the other type. This is the case, either when the surface layer consists of both metals (*surface alloy*) or when a monometallic substrate is covered by one layer of atoms of a different metal (*adlayer*). This review will concentrate on adlayers in the monolayer range and ordered surface alloys which allow detailed studies of local effects with integrating surface science methods such as temperature programmed desorption (TPD), photoelectron spectroscopy or electron diffraction. Effects due to the surface morphology on a mesoscopic scale (≈100 Å), such as island boundary, particle size or spillover effects (cf [5]), are not considered in this review.

Locally, the energetics and kinetics of adsorption, desorption and reactions of molecules on a surface strongly depend on the bond formation between a small ensemble of surface atoms and the adsorbate and/or dissociation products [13–15]. The bond formation between surface metal atoms and molecules is governed by the binding energies, orientation and occupation of the molecular valence orbitals and the surface band structure [16]. For bimetallic surfaces the latter is, of course, determined by the coupling between the electronic states of the two metals involved [7, 8], which is often referred to as the *electronic factor* or *ligand effect* [15]. This coupling essentially determines to what extent charge transfer takes place between the two metals, i.e. how much substrate-related electronic states can contribute to a chemical bond

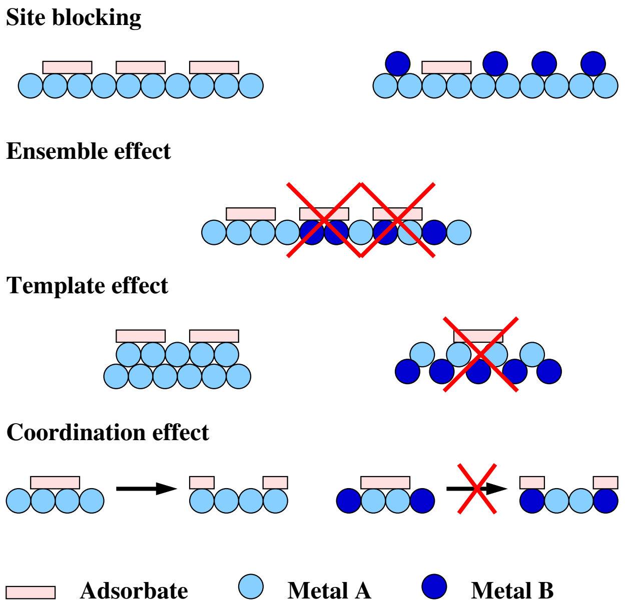

Figure 1. Geometric factors determining the adsorption and dissociation of molecules on bimetallic surfaces. See the text for explanation.

(This figure is in colour only in the electronic version)

at the surface of thin monometallic adlayers, and to what extent the electronic properties of single metal atoms are modified in surface alloys.

The electronic coupling depends upon:

- The *overlap in binding energies and the symmetries* of the relevant electronic states. There is usually a large overlap in binding energies for the sp-related bands of transition metals. The energy overlap in the d bands differs, however. For example, there is very little overlap between the narrow 3d bands of copper and nickel, but the copper 3d band overlaps fully with the much wider Ru 4d band [17]. Coupling is essentially impossible between transition metal d states and the low-lying d states of non-transition metals. We can therefore expect significant differences in the electronic structure of these bimetallic surfaces.
- The *lattice parameters* determine the coordination and the interatomic distances and thus the overlap of valence orbitals within the surface layer. Less overlap usually leads to a smaller band dispersion, which causes downward shifts in the mean binding energy for more than half-filled d bands [18]. In particular this geometrically induced shift of the d-band centre relative to the Fermi energy has been made responsible for changes in the reactivities of bimetallic compared to pure transition metal surfaces in a series of recent publications by Hammer and Nørskov *et al* [8, 9].

Another important factor is the *geometric factor*, i.e. the arrangement of surface atoms on a microscopic scale. This can influence the reactivity of the surface in many ways (see figure 1).

- *Site blocking:* metal atoms which can only form weak bonds with the adsorbate occupy possible adsorption sites where the molecule could form a stronger bond with the underlying substrate.

- *Ensemble effect:* a minimum number of adjacent surface atoms is needed to form the adsorption site. The removal of an atom or incorporation of another atom destroys the ensemble and changes the adsorption properties significantly.
- *Template effect:* a molecule requires an adsorption site of a certain shape or size. In the simplest case this could mean that a certain interatomic distance of the surface atoms is required. In more complex cases, the surface and the adsorbate can form a 'lock and key' system which is utilized, for example, in enantioselective catalysis [15].
- *Coordination effect:* a reaction (dissociation or association) requires a minimum number of adjacent adsorption sites for the reactants or reaction products. Otherwise the reaction cannot occur.

Since the arrangement of surface atoms influences the electronic structure of the surface and vice versa, it is in practice often impossible to discriminate between geometric and electronic effects. In the special case of flat monometallic adlayers, however, coordination and ensemble effects are *a priori* excluded so that changes in the surface reactivity must be attributed to electronic or template effects.

1.2. Adsorption of benzene

So far, the vast majority of studies on the reactivity of bimetallic surfaces has concentrated on the adsorption of diatomic molecules or atoms such as CO, NO, O and H. In particular CO has often been used as a probe molecule to study the surface termination and morphology [6, 19]. Because of their small size and/or their upright adsorption geometries these adsorbates are not affected by template effects: only site blocking, ensemble, and coordination effects can play a role. This is different for benzene. Due to its larger size and internal structure template effects can be expected to play a much more important role in the adsorption and dissociation on bimetallic surfaces, besides the other geometric and electronic factors.

The adsorption of benzene on monometallic transition metal single-crystal surfaces has been studied in great detail over the past two decades [12, 20]. By surface science standards benzene is a relatively large molecule but, due to its high symmetry, it has still a rather simple electronic structure with HOMO and LUMO states derived from π-orbitals which are localized near the C_6 ring. Electron spectroscopic studies and *ab initio* calculations show that the coupling of these orbitals with substrate d electrons is the main contribution to the formation of the surface bond [20–22]. This is the reason why benzene is usually found to chemisorb with the C_6 ring parallel to the surface plane of close packed surfaces, e.g. fcc(111) [12, 20], because the overlap between molecular π-orbitals and surface d electronic states is maximized this way. On more open surfaces, e.g. reconstructed fcc(110), the molecule usually adsorbs parallel to the closest packed facets, i.e. not parallel to the macroscopic surface plane, for the same reason [12, 23]. Experimental indications for the strength of the surface bond are the molecular desorption temperatures in TPD and differential (bonding) shifts with respect to the gas phase in the binding energies of the molecular π-orbitals $1a_{2u}$ and $1e_{1g}$ as measured in UV photoelectron spectroscopy (UPS).

Upon adsorption at low temperatures (below 250 K) benzene does not dissociate on the late transition metals (group VIII-B and I-B) for which most studies have been carried out. Annealing, however, causes decomposition of the molecule on all transition metals except for the coinage metals (I-B: Cu, Ag, Au). The decomposition process involves several hydrocarbon intermediates which eventually dissociate into carbon atoms, left behind on the surface, and molecular hydrogen which desorbs instantaneously. We can expect the most drastic changes in the reactivity for I-B – VIII-B bimetallic surfaces, depending on the surface composition and termination or on the combination of transition metals with non-transition metals.

2. Adsorption on surface alloys

Surface alloys are either the surfaces of bulk alloy single crystals or can be produced by the deposition of a second metal onto the surface of a monometallic single crystal [1, 6]. By the definition we are using throughout this review, in a 'true' bimetallic surface alloy both types of metals are exposed to the vacuum, allowing them direct contact with adsorbed molecules. The surface metal atoms can either be arranged periodically or randomly, forming ordered or disordered surface alloys, respectively. Of particular importance to heterogeneous catalysis is the fact that, on surface alloys, site blocking, ensemble, and coordination effects can play a dominant role which can change the catalytic behaviour of these surfaces completely, as compared to the monometallic surfaces of the constituents. This has attracted the interest of many researchers since the early 1950s [13–15, 24]. (A historical review including a discussion of modern concepts is given in [5].)

In many cases it is thermodynamically favourable when the surface is covered by only one type of metal atom, namely those which have the lower surface free energy. This leads to an essentially monometallic surface layer with atoms of the other metal only in the second and consecutive layers. These surfaces are the subject of the next section. Also, when large islands are formed due to attractive interactions between metal atoms deposited onto a metal substrate, these bimetallic surfaces do not fall into the category of surface alloys. The local adsorption behaviour on large islands is the same as on the fully covered surface, whereas extended areas between the islands behave like the clean substrate surface. Bimetallic effects occur only on a small fraction of the surface near the island boundaries. (For a recent review on island growth see [25].) This small fraction of the surface area can still dominate the catalytic activity of such surfaces: however, very little is known about the adsorption geometry, bond strength, etc at these sites.

2.1. 'True' surface alloys

A number of studies concentrate on the formation of benzene via acetylene cyclotrimerization or other reaction pathways on surface alloys of Pd–Au [26, 27], Pt–Cu [28], Pd–W [29, 30] and Pt–Sn [31, 32]. Sn/Pt(111) is the only surface alloy for which there is detailed information available about the adsorption geometry and bond strength of adsorbed benzene.

Deposition of Sn onto Pt(111) leads to the formation of two ordered surface alloys with surface stoichiometries of Pt_2Sn (forming a $p(\sqrt{3} \times \sqrt{3})R30°$ superlattice) and Pt_3Sn (forming a $p(2 \times 2)$ superlattice), depending on the annealing temperature [33, 34] (see figure 2). When benzene is adsorbed on Pt(111) at low temperatures, TPD shows a sharp multilayer desorption peak around 170 K and two broad molecular features between 300 and 500 K. After annealing to 500 K desorption of hydrogen is observed indicating the decomposition of benzene. The same experiment with either of the two ordered Sn/Pt(111) surface alloys shows no significant hydrogen desorption, i.e. the decomposition of benzene is inhibited and essentially all molecular desorption is shifted downwards in temperature below around 200 K [33, 34]. High resolution electron energy loss spectroscopy (HREELS) and UPS data for benzene adsorbed on both surface alloys show great similarities with benzene in the condensed (multilayer) phase, which indicates that the molecule is essentially physisorbed on these surfaces [34]. These changes in the adsorption behaviour with respect to Pt(111) are too strong to be explained only by changes in the electronic structure of the surface, namely the filling of the Pt 5d band due to charge transfer between Sn and Pt atoms. This kind of charge transfer has been observed by photoelectron spectroscopy for the very similar Sn/Pd(111) surface alloys [35]. Even with a completely filled Pt 5d band one would still expect the

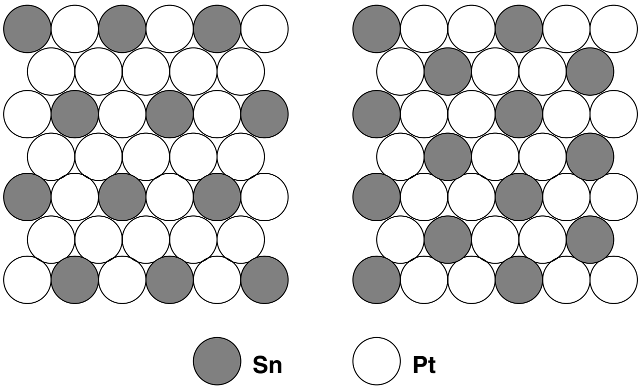

Figure 2. Surface structures for the $p(2 \times 2)$ (left) and $p(\sqrt{3} \times \sqrt{3})R30°$ (right) Sn/Pt(111) surface alloy [33].

molecules to be chemisorbed. The suppression of benzene chemisorption is due to the fact that the Pt_3Sn and Pt_2Sn surfaces do not contain the Pt ensembles needed for benzene molecules to chemisorb. Campbell *et al* [36, 37] found that the minimum ensemble on Pt(111) is about 6 Pt atoms for chemisorption (ensemble effect) and 6–11 Pt atoms for dehydrogenation of benzene (coordination effect). The $p(\sqrt{3} \times \sqrt{3})R30°$ and $p(2 \times 2)$ Sn/Pt(111) surface alloys, however, provide only ensembles of 2 and 3 Pt atoms, respectively (see figure 2).

This is also one of the reasons why the cyclotrimerization of acetylene to benzene is catalysed by these surface alloys but not by Pt(111): the smaller acetylene molecule can chemisorb on the alloy surface but its decomposition is substantially reduced due to the same coordination effect; the reaction product, benzene, is weakly adsorbed, i.e. it desorbs immediately after the reaction and does not block sites for further acetylene adsorption [31, 32].

2.2. *Ordered adlayers of non-transition metals*

Another group of bimetallic surfaces are monometallic substrates with an adlayer of a different kind of metal atom, forming a superlattice with a periodicity larger than that of the substrate surface lattice. Such superlattices are formed when there is a repulsive interaction between the adlayer atoms, such as for alkali metals. These are not surface alloys in a strict sense since the two metals are in separate layers. However, both types of atoms are exposed and could, in principle, interact with adsorbate molecules. Benzene adsorption has been studied for Bi/Pt(111) [36–38], Cs/Pt(111) [39] and K/Ni(111) [40].

The studies on Bi/Pt(111) and Cs/Pt(111) cover a wide range of admetal coverages up to the saturation of the adlayer (0.56 ML for bismuth and 0.41 ML for caesium), where the systems go through several ordered phases. Both systems show a very similar behaviour. As can be seen from figure 3, the TPD spectra after benzene adsorption onto very small admetal coverages are essentially identical to the ones for Pt(111). After a certain threshold coverage is reached, the maximum desorption temperature for intact benzene decreases and dissociation is more and more suppressed with increasing coverage. Some of the key data are also listed in table 1. For admetal coverages exceeding about half the saturation coverage no dissociation is observed any longer and the molecular desorption peak coincides with the multilayer desorption peak. X-ray photoelectron spectroscopy (XPS) for benzene on Bi/Pt(111) shows a shift of +1.1 eV in the C 1s binding energy with increasing Bi coverage, indicating a transition from chemisorption to physisorbed molecules which is in agreement with the low desorption temperature [37].

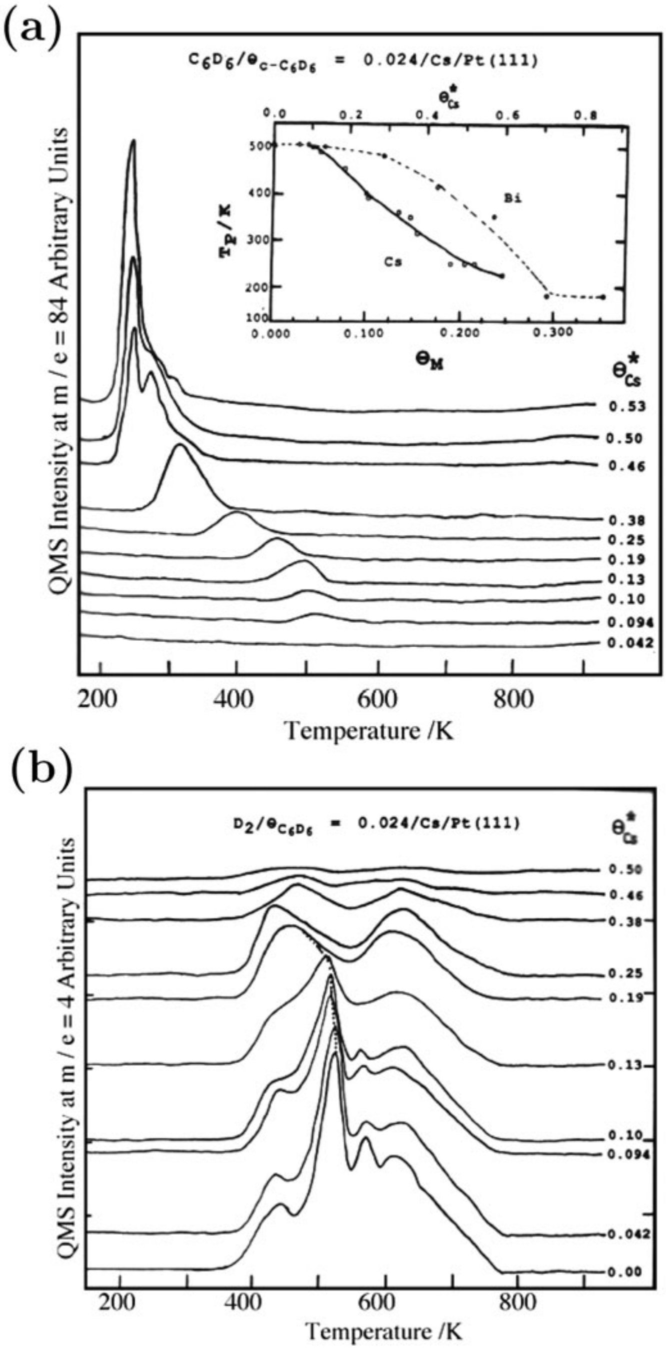

Figure 3. Top: the effect of increasing Cs coverage on Pt(111) on the molecular desorption of C_6D_6 for a fixed 0.1 L C_6D_6 exposure at about 100 K. (Inset: effect of Cs and Bi coverage on the peak desorption temperature of the molecular desorption peak; Θ_M corresponds to the number of admetal atoms per surface Pt atom.) Bottom: the effect of increasing Cs coverage on Pt(111) on the D_2 TPD spectra for a fixed 0.1 L exposure of C_6D_6 at about 100 K. Reproduced with permission from [39]. Copyright 1991 Am. Chem. Soc.

Table 1. Selected data regarding the adsorption and dissociation of chemisorbed benzene layers on different hexagonal mono- and bimetallic surfaces. The bonding shift refers to the differential shifts in binding energies of the $1a_{2u}$ and $1e_{1g}$ benzene orbitals with respect to the other molecular orbitals which are not involved in the surface bond. For an explanation of the orientation symbols σ_d and σ_v see figure 4. The letters in the first column refer to the TPD spectra in figure 5.

Surface	Lattice constant (Å)	Benzene coverage (ML)	Max. molecular des. temperature (K)	Dissociation	Bonding shift (eV) ($1a_{2u}$ and $1e_{1g}$)	Orientation	Structural technique references
			Ordered alloys				
$Pt_2Sn/Pt(111)$	2.77, p($\sqrt{3} \times \sqrt{3}$)R30°	Sat.	180	No	0.0	(Not rep.)	[34]
		Sat.	500^a	No			[33]
$Pt_3Sn/Pt(111)$	2.77, p(2 × 2)	Sat.	200	No	0.0	(Not rep.)	[34]
		Sat.	350^a	No			[33]
Pt(111)	2.77	0.16	500	Yes	1.1	σ_d	UPS, LEED [34, 62]
			Ordered admetal layers				
0.25 ML Bi/Pt(111)	2.77, p(2 × 2)	Sat.	400	Yes	(Not rep.)	(Not rep.)	[37, 38]
0.5 ML Bi/Pt(111)	2.77, c(4 × 2)	Sat.	180	No	(Not rep.)	(Not rep.)	[37, 38]
0.41 ML Cs/Pt(111)	2.77	Sat.	220	No	(Not rep.)	(Not rep.)	[39]
0.34 ML K/Ni(111)	2.49, p($\sqrt{3} \times \sqrt{3}$)R30°	0.14	142	No	(Not rep.)	(Not rep.)	[40]

Table 1. (Continued.)

Surface	Lattice constant (Å)	Benzene coverage (ML)	Max. molecular des. temperature (K)	Dissociation	Bonding shift (eV) ($1a_{2u}$ and $1e_{1g}$)	Orientation	Structural technique references
			Pseudomorphic monolayers				
(a) Cu/Ni(111)	2.49 (−2.3%)	0.08	240	No	0.3	No azim. orientation	ARUPS [51]
(b) Ni(111)	2.49	0.14	450	Yes	1.4	σ_d	ARUPS [59]
Ni(111)	2.49	0.10	450	Yes	1.5	σ_v	ARUPS [59, 63]
(c) Ni/Cu(111) (adlayer)	2.55 (+2.4%)	0.14	—	Yes	1.4	σ_v	ARUPS [52]
(d) Cu/Ni/Cu(111) (sublayer)	2.55 (+2.4%)	0.10	250	No	0.3	No azim. orientation	ARUPS [52]
(e) Cu(111)	2.55	0.09	240	No	0.3	No azim. orientation	ARUPS [51]
(f) Cu/Ru(0001)	2.71 (+6.3%)	0.13	340	No	1.1	σ_d	ARUPS [17]
Pd/Ru(0001)	2.71 (−1.5%)	(Sat.)	440	(Not rep.)		(Not rep.)	[26]
(g) Ru(0001)	2.71	0.14	390	Yes	1.3	σ_v	ARUPS [17]
Pd(111)	2.75	(Sat.)	580	Yes	1.5	Flat, no azim. rep.	ARUPS [64, 65]

[a] Very small signal above 200 K.

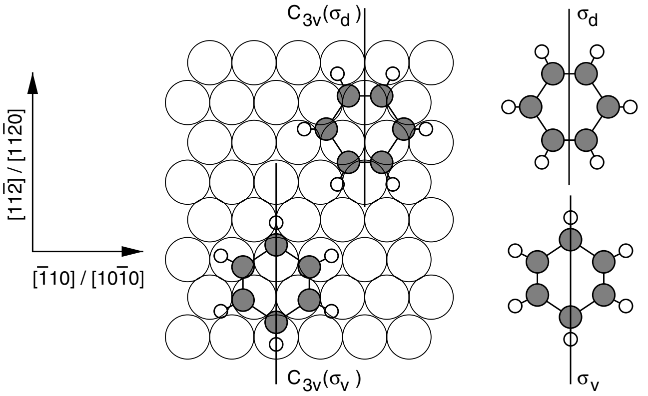

Figure 4. Schematic drawing of the two possible orientations of benzene which lead to the highest possible symmetry, C_{3v}, of the adsorption complex on a hexagonal surface. Top: $C_{3v}(\sigma_d)$; C–C and C–H bonds parallel to the close packed rows ($[\bar{1}10]$ in fcc(111) and $[10\bar{1}0]$ in hcp(0001)). Bottom: $C_{3v}(\sigma_v)$; C–C and C–H bonds perpendicular to the close packed rows ($[11\bar{2}]$ in fcc(111) and $[11\bar{2}0]$ in hcp(0001)) [52].

Campbell *et al* [36–39] interpreted these findings in the following way: due to the high mobility of the admetal atoms at low coverages, the benzene molecules can push them away from their original positions and create the Pt ensemble size needed for chemisorption. The repulsive interaction between the admetal atoms causes a decrease in the energy gain upon adsorption, which leads to the observed fall in the desorption temperature. The effect is greater for Cs which has a larger dipole moment than Bi and, hence, causes stronger repulsion between the admetal atoms. Since a larger ensemble size is needed for dissociation, this is reduced already at intermediate coverages. For high adlayer coverages the repulsion is too strong to create a large enough Pt ensemble. Benzene cannot form chemisorption bonds with the adlayer atoms due to the absence of d states near the Fermi level. Consequently the desorption temperature is shifted towards the desorption temperature of physisorbed multilayers.

Adsorption on K/Ni(111) has only been studied for the saturated potassium adlayer (0.34 ML) [40]. The TPD results are in agreement with the findings for the saturated layers of the above systems: the molecular desorption signal appears at the multilayer desorption temperature (142 K) for all benzene coverages and dissociation is suppressed.

All cases discussed in this section are bimetallic surfaces involving a group VIII transition metal and a non-transition metal with completely filled low-lying d states. The latter metals form very weak bonds with benzene and there is no coupling between the d states of these metals. Therefore the drastic changes in the adsorption and dissociation behaviour with respect to the monometallic transition metal surfaces are essentially due to site blocking and ensemble effects. Electronic effects due to charge transfer play only a secondary role.

3. Adsorption and dissociation of benzene on pseudomorphic monolayers

Artificially produced monometallic pseudomorphic adlayers on a substrate consisting of a different kind of metal atom may seem somewhat unrelated to bimetallic catalyst surfaces at first sight. However, for many alloys it is thermodynamically favourable when the surface is terminated by only one metal, namely the one with the lower surface free energy (*surface segregation* [5]). Well-known examples, which are important in catalysis, are Cu–Ni [41]

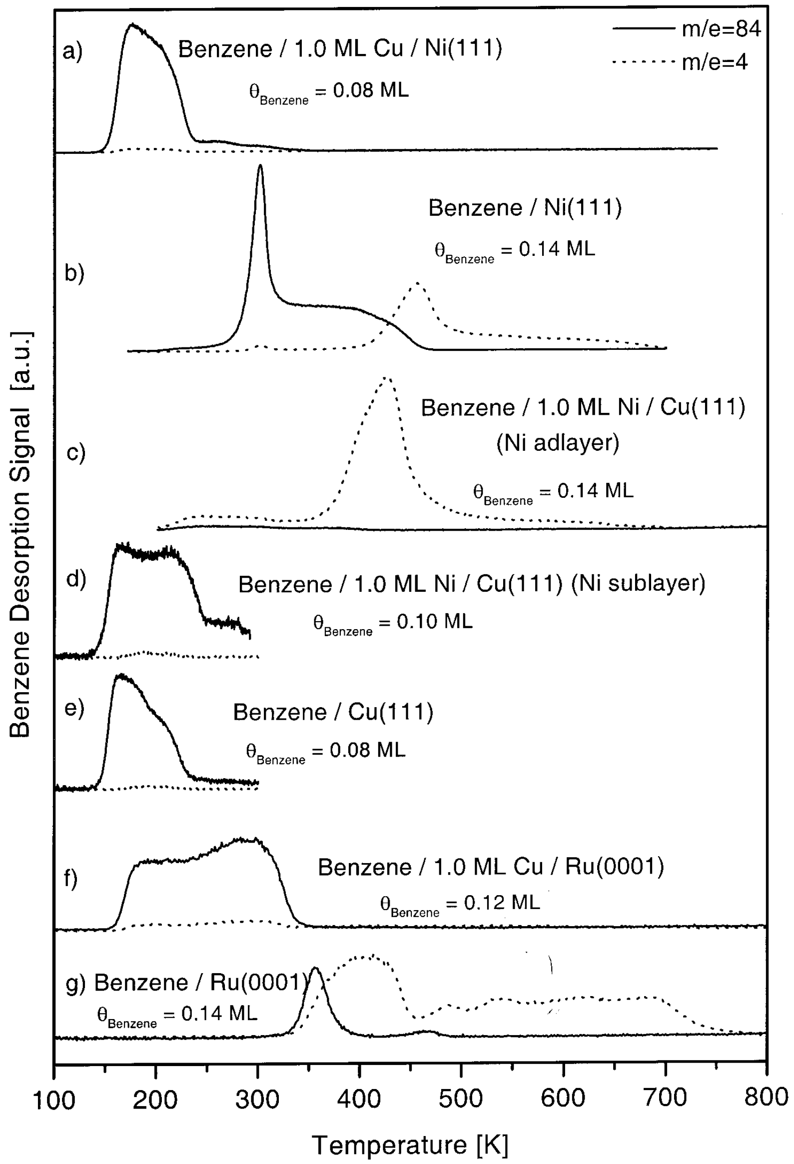

Figure 5. TPD spectra of chemisorbed benzene layers on different mono- and bimetallic surfaces: (a) 1 ML Cu/Ni(111); (b) clean Ni(111); (c) 1 ML Ni/Cu(111) adlayer; (d) 1 ML Ni/Cu(111) sublayer; (e) clean Cu(111); (f) 1 ML Cu/Ru(0001); (g) clean Ru(0001); full curve: C_6D_6 desorption ($m/e = 84$); dotted curve: D_2 desorption ($m/e = 4$) [52].

(Cu-terminated) and Cu–Zn [42] (Zn-terminated). For low bulk concentrations of the segregating component, the surface layer is essentially a pseudomorphic monometallic layer on a substrate dominated by the majority component. According to theoretical predictions by Ruban *et al* [43] this type of bimetallic surface should be found under uhv conditions more often than true surface alloys. Certainly in the literature there are more experimental surface science studies on pseudomorphic monolayers and related thin film systems than on true surface alloys. Under reaction conditions (high pressure, high temperature), however, the surface is covered by reactant molecules and the metal atoms are usually mobile enough to adjust to the thermodynamically favourable configuration, which is now determined by the bond energy between the adsorbed molecules and the surface metal atoms. This may suppress or even reverse clean surface segregation effects (see, e.g., [44] for Cu–Ni).

When the surface is fully covered by a monometallic pseudomorphic layer of atoms different from the substrate atoms, site blocking, ensemble and coordination effects are *a priori* excluded from the arsenal of bimetallic effects. Only template effects (change of lattice parameters) and electronic effects can play a role in determining the adsorption and dissociation behaviour of benzene on such surfaces. As mentioned earlier, the surface bond is dominated by the interaction between the metal d states and the π-orbitals of the molecule [20–22, 45, 46] and the exact adsorption geometry and the direction of charge transfer depend very much on the local details of the electronic structure at the surface. It is therefore important to have information about the adsorption geometry in addition to kinetic and spectroscopic data.

Angle resolved UV photoelectron spectroscopy (ARUPS) has proved to be a valuable technique for gathering geometrical information about the adsorption of benzene on bimetallic surfaces. No information about bond lengths and adsorption sites can be gained from this method but, by applying symmetry selection rules, one can determine the orientation of the molecule with respect to the underlying surface [47–50], even when the molecules form disordered layers on the surface. With ARUPS the orientation of benzene on a number of bimetallic surfaces has recently been determined, namely on Cu/Ni(111) [51], Ni/Cu(111) adlayer and sublayer [52] and Cu/Ru(0001) [17]. These results are included in table 1 together with the data for monometallic surfaces relevant to these systems; an explanation of the orientation symbols is given in figure 4. For a correlation with the reactivity of these surfaces the TPD spectra of the chemisorbed benzene layers are shown in figure 5. The spectra for $m/e = 84$ show the desorption of intact deuterated benzene (C_6D_6) while the spectra for $m/e = 4$ (D_2) indicate if and at what temperature dissociation occurs. (Note: C_6D_6 was used in the experiments in order to discriminate the dissociation product D_2 from background hydrogen H_2, which is the main residual gas in uhv systems.)

No azimuthal ordering is found at 80 K for the copper-terminated surfaces Cu/Ni(111), Ni/Cu(111) sublayer (with a Cu/Ni/Cu stacking of layers) and Cu(111). This azimuthal disorder can either be static, due to equal or similar bond energies in different adsorption geometries, or dynamical, due to frustrated rotations in a shallow potential minimum at the energetically favoured adsorption site. The latter option seems more likely because a tendency towards azimuthal order is observed at 30 K on Cu(111) [53]. The low desorption temperatures between 150 and 250 K for these surfaces (curves (a), (d) and (e) in figure 5), the small chemical shift of 0.3 eV and the fact that no dissociation occurs indicate that the benzene–surface bond is weak for these copper-terminated surfaces. The width of the molecular desorption features can be understood in terms of further reduction of the adsorption energy due to repulsive lateral interactions at higher coverage [54, 55].

On the copper-terminated Cu/Ru(0001) surface, however, benzene orders azimuthally assuming a σ_d orientation which goes along with an increase in the maximum desorption temperature by about 100 K with respect to Cu(111) (curve (f) in figure 5). This increase in the surface bond strength and the well-defined azimuthal orientation at 80 K is caused by the large expansion (+6.3%) of the Cu overlayer lattice with respect to the Cu(111) surface and a strong coupling of Ru 4d and Cu 3d electronic states [17, 56, 57]. This is not the case for Cu/Ni(111) where the Cu and Ni d bands show very little coupling [51, 58]. It is interesting to note that the compression of the Pd monolayer by -1.5% on Ru(0001) has the opposite effect than the expansion of Cu/Ru(0001). For Pd/Ru(0001) the maximum molecular desorption temperature decreases by 140 K with respect to Pd(111) [26] (see table 1). Details of the electronic structure for this system are, however, not known.

Dissociation, indicated by the production and desorption of hydrogen, is only seen for the Ni- and Ru-terminated surfaces included in figure 5. Such a behaviour is expected from the trend observed on single-crystal surfaces, namely that coinage metals do not catalyse the decomposition of benzene while group VIII transition metals do. If one compares the TPD spectra of Ni(111) (b) and the Ni/Cu(111) adlayer (c) in figure 5, the latter surface seems to be much more reactive since no molecular desorption of benzene is observed at all, i.e. all adsorbed benzene dissociates, whereas on Ni(111) about 40% of the initially chemisorbed molecules desorb intact. It is known that the Ni/Cu(111) surface is metastable and restructures into a thermodynamically more stable arrangement where a monolayer of copper atoms covers the Ni layer, driven by the lower surface free energy of copper [52] ('Ni sublayer', also included in figure 5(d) and table 1). This transition takes place at temperatures above 450 K, where also the D_2 signal, indicating dissociation, is observed. Desorption in this temperature range does not necessarily, therefore, resemble the static properties of this surface and the difference in the dissociation behaviour could, in principle, be entirely driven by the restructuring of the bimetallic surface. However, molecular desorption on Ni(111) starts already below 300 K and should therefore also be observed on the Ni/Cu(111) adlayer if the bonding situation was similar.

Another decisive difference between the saturated benzene layers on these two surfaces is the different azimuthal orientations: σ_d on Ni(111) and σ_v on the Ni/Cu(111) adlayer. The orientation on the Ni adlayer is the same as for low coverages of benzene on Ni(111), which means that this is the preferred adsorption configuration in the absence of lateral interactions. It has been argued earlier that the rotated σ_d orientation in the saturated layer on Ni(111) is due to a steric effect [59]. With this orientation and the $p(\sqrt{7} \times \sqrt{7})R19°$ overlayer lattice of the saturated benzene layer on Ni(111) the C–H bonds point towards the gaps between two hydrogen atoms of their neighbouring molecules, as shown in figure 6(a), whereas in the σ_v orientation the C–H bonds would point towards each other (figure 6(b)). Thus the σ_d reduces the lateral repulsive interaction between the molecules at the expense of occupying a less favourable site [59]. In order to illustrate this, the approximate van der Waals shapes of the molecules have been included in the diagrams of figure 6. Since the Ni adlayer lattice on Cu(111) is expanded by +2.4% with respect to the Ni(111) surface lattice, there is slightly more space between the molecules if they form the same close packed $p(\sqrt{7} \times \sqrt{7})R19°$ local arrangement. It seems that this expansion is enough to reduce the lateral interaction between the molecules sufficiently so that the σ_v orientation which forms the stronger surface bond can be assumed even at saturation coverage which can be considered as a template effect.

This σ_v orientation is also the one from which the molecules dissociate on Ni(111) at low coverage: it therefore appears to be the 'reactive orientation' of benzene on both close-packed Ni-terminated surfaces. Complete dissociation of the saturated chemisorbed layer occurs on Ni/Cu(111) because this orientation is assumed at saturation coverage while on Ni(111) some of the benzene has to desorb intact before the remaining molecules can relax into the reactive orientation from which they then can dissociate [52]. In order to obtain a complete picture, however, one needs to know the *adsorption site* in addition to the orientation. This latter information is known from photoelectron diffraction (PhD) and low energy electron diffraction (LEED) studies for the saturated $p(\sqrt{7} \times \sqrt{7})R19°$ benzene layer and the dilute layer on Ni(111) to be the hcp and bridge sites, respectively [60, 61]. For Ni/Cu(111) no surface crystallographic data are available but by analogy one can probably assume that it is the same as for low coverages on Ni(111), i.e. the bridge site, as depicted in figure 6(b).

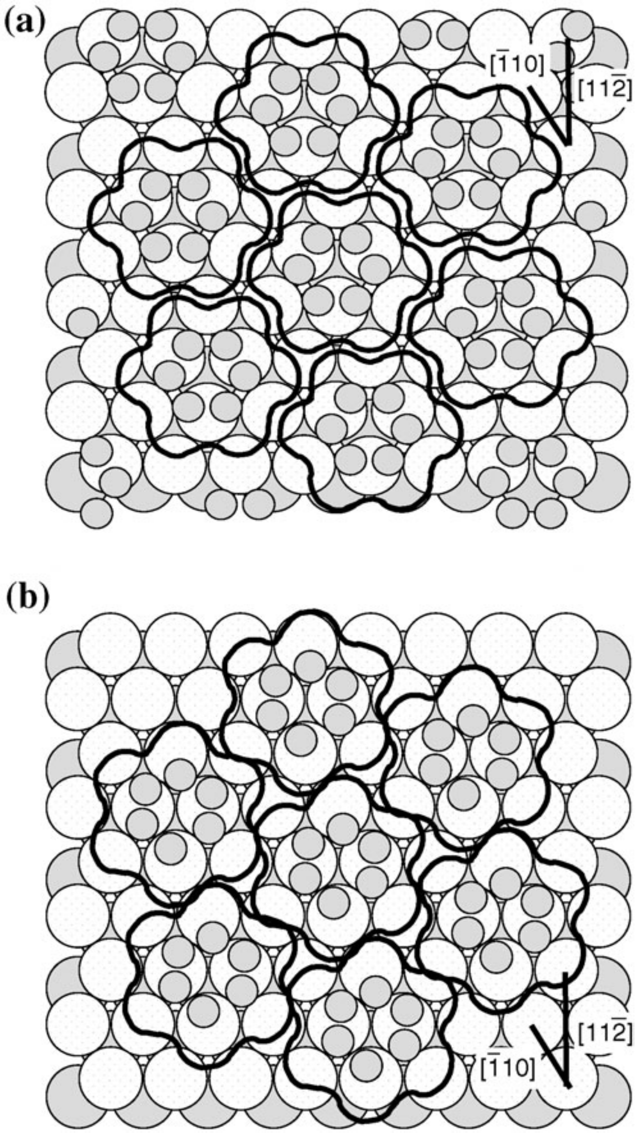

Figure 6. Benzene molecules in a local p($\sqrt{7} \times \sqrt{7}$)R30° arrangement for two different azimuthal orientations: (a) σ_d, hcp site (b) σ_v, bridge site. The lines around the C_6 rings indicate the approximate van der Waals shape of benzene.

4. Summary and conclusions

The data set available for benzene adsorption on bimetallic surfaces is still too incomplete to derive unambiguous trends throughout the periodic table. But a few conclusions can be made at this stage which are very likely to hold even when further data become available.

For combinations of *transition metals and non-transition metals* (I-A: K, Cs; IV-A: Sn; V-A: Bi) the main effect is the blocking of adsorption sites by the non-transition metal. Electronic effects play a minor role. Benzene requires a minimum ensemble size for chemisorption and dissociation (6 and 6–11, respectively, for Pt(111)). If this ensemble is not available dissociation and chemisorption are suppressed.

For combinations of *two transition metals* the surface termination determines the gross chemical behaviour. Changes in the electronic structure and small changes in the surface geometry due to lattice expansion/compression and coupling of electronic states can modify the bond strength to some extent.

Like for monometallic single crystals, surfaces terminated by coinage metals (I-B: Cu) do not catalyse the dissociation of benzene. The degree of dissociation on VIII-B-terminated surfaces (Ni, Ru, Pd) depends on the details of the electronic structure and/or adsorption geometry.

There is still a great demand for more data, especially about the adsorption behaviour of benzene on surfaces which are known to be good catalysts for benzene formation. With regards to the dissociation of benzene it will be worthwhile to investigate further the influence of the adsorption geometry on the dissociation probability. This will eventually lead to a more detailed insight into the dissociation mechanism of benzene in general.

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