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Surface Science and Catalysis [and Discussion]

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Surface science and catalysis

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Modern surface science studies have explored a large number of metal catalyst systems. Three classes of catalytic reactions can be identified: (1) those that occur over the metal surface; (2) reactions that take place on top of a strongly adsorbed overlayer and (3) reactions that occur on coadsorbate modified surfaces. Case histories for each class are presented.

The first class of reactions is structure sensitive, and rough surfaces are needed for high reactivity. Ammonia synthesis, H_2/D_2 exchange and complex hydrocarbon reaction studies all indicate the importance of high coordination sites that are present on atomically rough, open crystal surfaces, mostly in the second layer. A model is presented that correlates increased charge fluctuations at these sites with enhanced catalytic activity.

The second class of reactions includes ethylene hydrogenation. It occurs via hydrogen transfer through a tenaciously held ethylidyne overlayer to weakly adsorbed ethylene molecules on top of this layer.

Most catalytic reactions occur on coadsorbate modified metal surfaces. Sulphur, potassium, carbonaceous fragments and other metal constituents are employed most frequently as surface modifiers. These additives block sites and alter the bonding of the reactants, thereby changing the reaction paths. Their effects will be demonstrated through discussions of the CO/benzene, S/thiophene and CO/K interactions.

Introduction

The mating of surface science and heterogeneous catalysis has induced a rapid growth of catalysis science over the past 10 years. In this lecture I shall present a new view of catalytic reactions that emerges from these studies. This perspective builds on decades of catalytic investigations that determined turnover rates for a wide variety of reactions in the temperature range that has been found technologically useful (Davis 1982). These are shown for hydrocarbon reactions over platinum in figure 1. Turnover rates between 10^{-4} and 10^{2} molecules per site per second are used in the various technologies, and thus the temperature employed is adjusted to obtain the desired rates. The turnover rates are usually calculated by dividing the rate by the total number of surface atoms. So it presents a conservative estimate of the rate, which may be an order of magnitude higher if the concentration of active sites is 10% of the total number of surface sites. The more complex isomerization, cyclization, dehydrocyclization, and hydrogenolysis reactions have activation energies in the range of 35–45 kcal mol^{-1}† and thus high temperatures are required to make them at the desired rates. Hydrogenation has activation energies of 6–12 kcal mol^{-1} and therefore may be made at high rates at 300 K or below (Somorjai 1981). So there are at least two classes of catalytic reactions that are effected at high and at low temperatures under very different reaction conditions.

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† 1 kcal = 4.184 kJ.

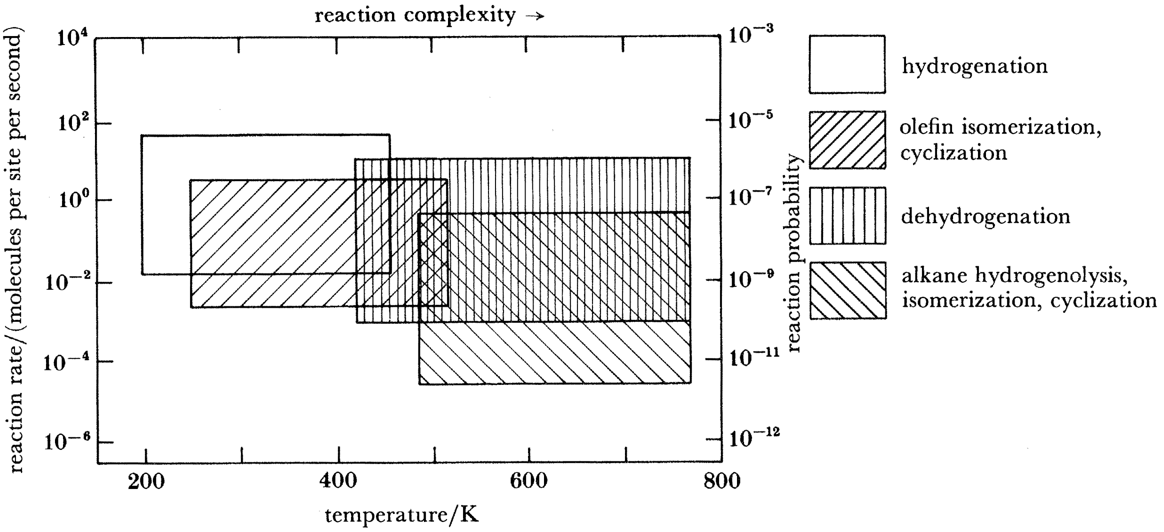

FIGURE 1. Block diagram for hydrocarbon conversion over platinum catalysts showing the approximate range of reaction rates and temperature régimes that are most commonly studied.

Surface science studies of catalysts are usually made by either using the real, high surface-area (*ca.* 10^2 m^2 g^{-1}) system or a low surface-area (*ca.* 1 cm^2 g^{-1}) model system. The most frequently used techniques for surface studies of catalysts are listed in table 1. Among them, infrared spectroscopy, solid state n.m.r. and X-ray photoelectron spectroscopies appear to be the most frequently employed for studies of real, high surface-area catalysts. Extended X-ray absorption fine structure and near-edge X-ray extended absorption fine structure measurements that require high-intensity synchrotron radiation provide very valuable information on the inter-atomic distances and number of nearest neighbours of small catalyst particles dispersed on high surface-area supports. Electron and ion scattering techniques are especially useful for studies of model, small-area catalyst systems because of their high surface sensitivity (Somorjai 1981). Small-area catalysts can be well characterized in ultra-high vacuum (*ca.* 10^{-9} Torr†), and then placed in a high-pressure environment (1–10^2 atm‡) by low-pressure–high-pressure instrumentation that is displayed in figure 2. At high pressures the reaction kinetics are

TABLE 1. FREQUENTLY USED TECHNIQUES OF SURFACE SCIENCE FOR STUDIES OF CATALYSTS

electron scattering
electron spectroscopy (X.p.s., h.r.e.e.l.s., A.e.s.)
low energy electron diffraction (l.e.e.d.)
electron microscopy
photon scattering (high and low intensities)
spectroscopy (i.L., F.t.i.r., Raman, solid state n.m.r., e.s.r., e.X.a.f.s., n.e.X.a.f.s., laser techniques)
grazing angle X-ray diffraction
molecule and ion scattering
molecular beam–surface interaction s.i.m.s., i.s.s.
other techniques
radiotracer labelling
Mössbauer spectroscopy
thermal desorption

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† 1 Torr ≈ 133.322 Pa. ‡ 1 atm = 101325 Pa.

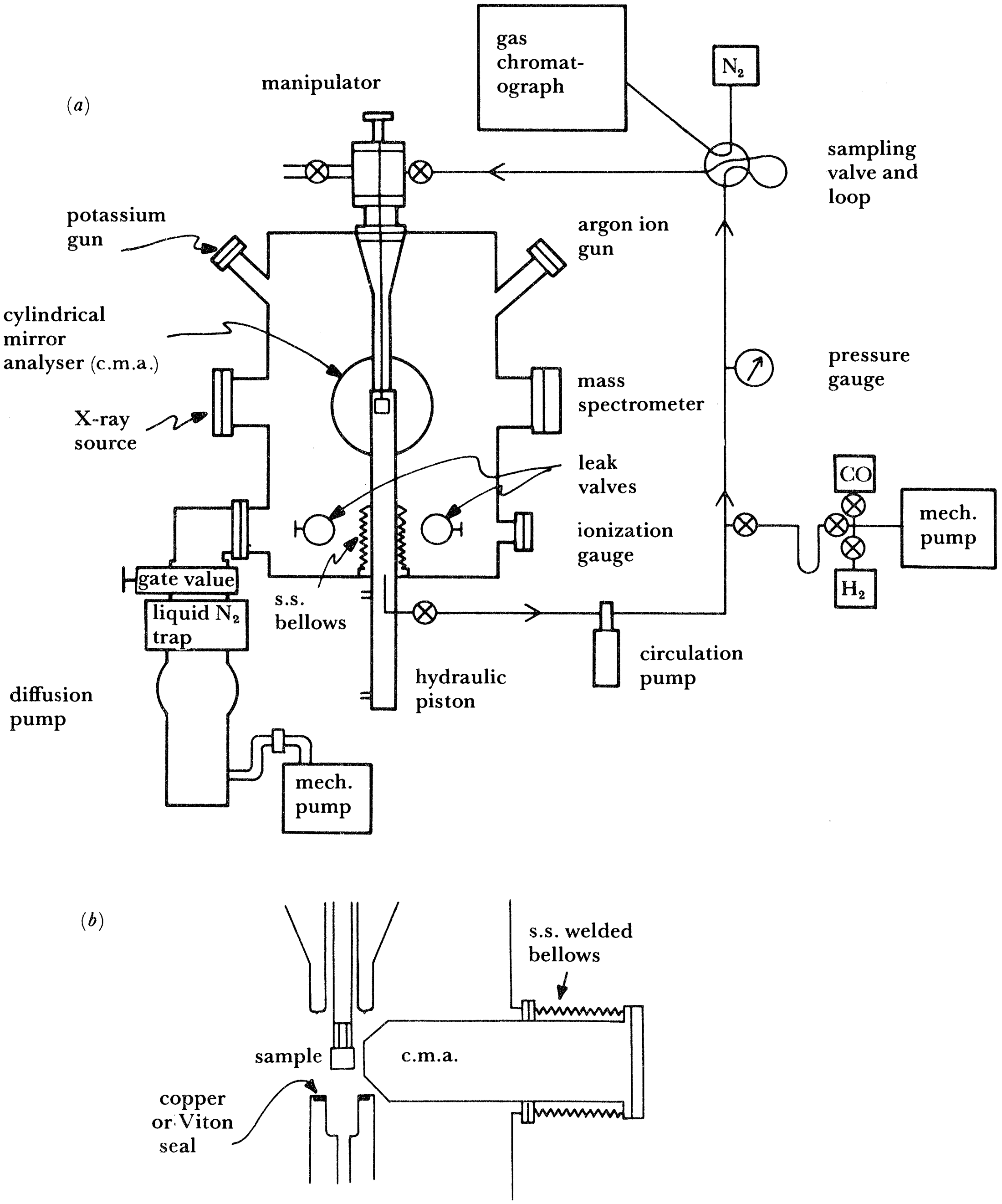


Figure 2. (*a*) Schematic representation of the experimental apparatus used to make the catalytic reaction rate studies on small-area single-crystal or polycrystalline surfaces at low and high pressures in the 10^{-7} to 10^{+4} Torr range. (*b*) Side view with high-pressure cell open.

monitored by gas chromatography, and easy cycling between low pressure and high pressures permits intermittent surface analysis of the catalyst (Cabrera *et al.* 1982). The use of high surface-area catalysts in combined catalysis and surface science studies allows us to study directly the real, working catalysts. Its drawback is the difficulty to characterize well such a complex high surface-area heterogeneous system. Model single-crystal or similar surfaces are

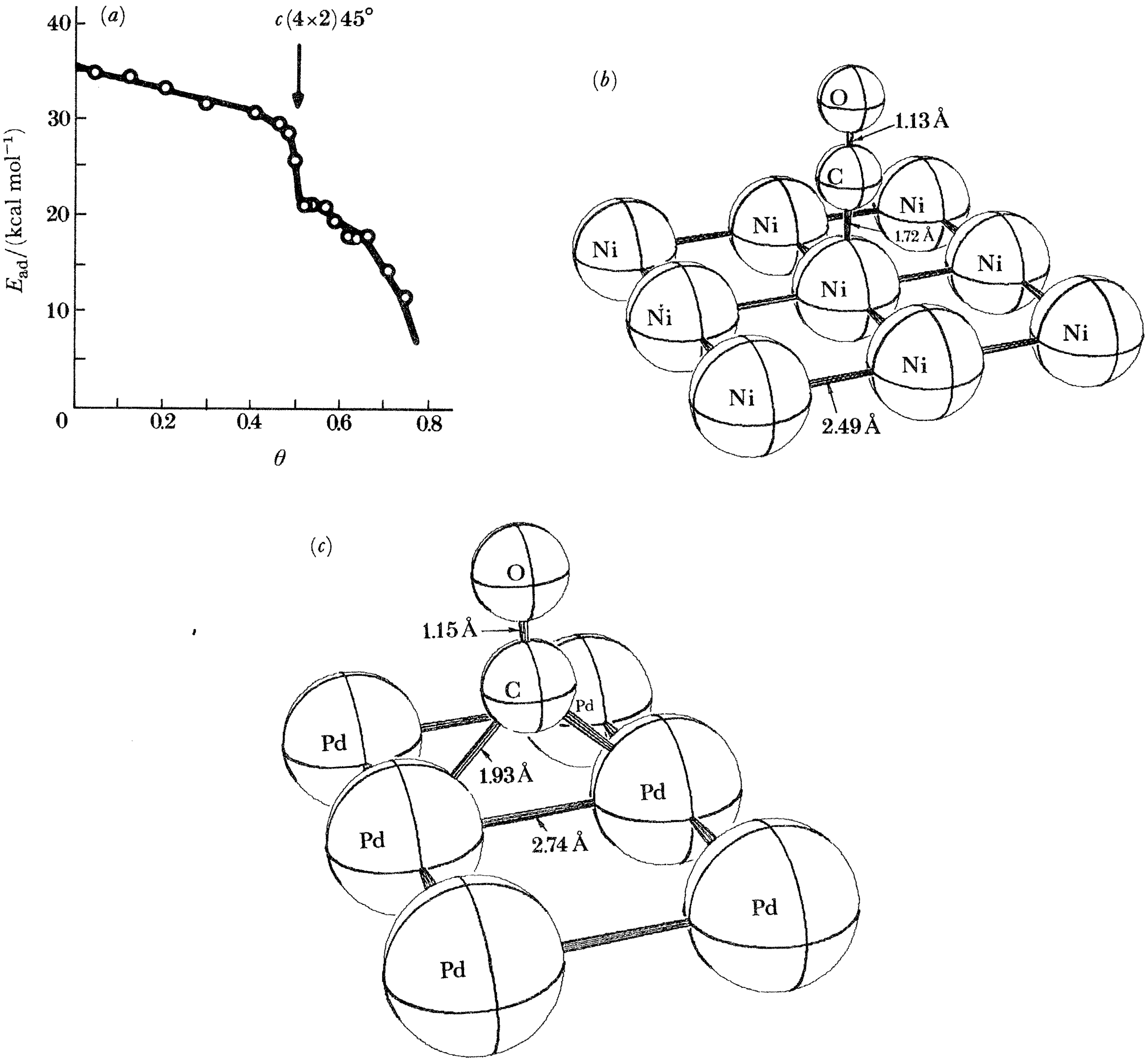


FIGURE 3 (*a–c*). For description see opposite.

TABLE 2. SURFACE SCIENCE STUDIES OF CATALYST SYSTEMS

(1) hydrogen–deuterium exchange by platinum
(2) oxidation of carbon monoxide by platinum
(3) hydrogenation of ethylene by Pt, Rh
(4) ammonia synthesis by iron, rhenium
(5) hydrocarbon conversion by platinum (dehydrocyclization, isomerization, hydrogenolysis, hydrogenation, dehydrogenation)
(6) hydrogenation of carbon monoxide by transition metals (Fe, Ni, Rh, Ru, Rd, Co, Mo)
(7) partial oxidation of ethylene by silver and methanol by molybdenum oxide
(8) hydrosulphurization of tiophene by molybdenum

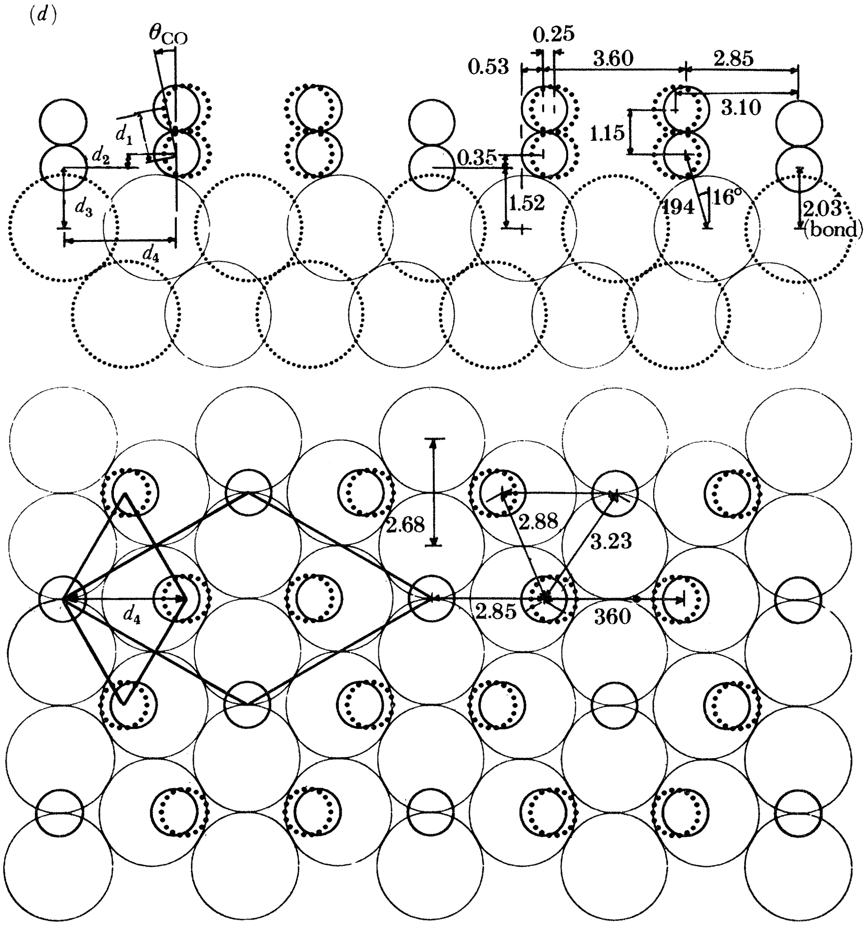


FIGURE 3. (*a*) Heat of adsorption for CO on the Pd(111) crystal face as a function of coverage (after Conrad *et al.* 1974). (*b*) Top-site bonding structure of carbon monoxide on Ni(100) from low-energy electron diffraction and electron spectroscopy studies. (*c*) Bridge-site adsorption structure of carbon monoxide on Pd(100) at a half monolayer coverage. (*d*) Structure determined by low-energy electron diffraction for a saturation coverage of carbon monoxide on Rh(111). Top and side views are shown. Large circles represent rhodium atoms while smaller ones correspond to carbon and oxygen atoms. Solid lines show the structure expected for hexagonal close packing of the carbon monoxide, while dotted circles depict the actual structure. All dimensions are given in ångström. Note that: d_1 is the C–O bond length; d_2 is the distance perpendicular to the C–O bond; d_3 is the distance parallel to the RhC bond; d_4 is the distance parallel to C–C.

much easier to characterize by the techniques of modern surface science. However, it is more difficult to correlate their catalytic behaviour or surface properties to the behaviour of the real, high-area catalyst systems.

There are several technologically important catalyst systems that have been subjected to combined surface science and kinetic studies. These are listed in table 2. The systems studied have been mostly metals. The results of these investigations suggest that there are three classes of catalytic reactions: (1) those that occur directly on the metal surface; (2) reactions that occur on top of a strongly bound layer of adsorbates in the second layer and (3) reactions that occur on coadsorbate-modified surfaces. I shall present examples of each of these reaction classes below.

There are major differences between the surface species that are usually studied by surface science at low pressures and those that are likely to be important surface species at high pressures during the catalytic reactions. This may be demonstrated in figure 3*a*, which shows data obtained in Professor Ertl's laboratory for the heat of adsorption of CO as a function of coverage over a Pd crystal surface (Conrad *et al.* 1974). At low coverages, the heat of adsorption per mole is high and these strongly adsorbed molecules are the subject of low-pressure surface science studies because of their stability that makes such studies easy. Their structures (Andersson *et al.* 1978 and Behm *et al.* 1979) are shown in figure 3*b*, *c*. At higher coverages the average heat of adsorption drops significantly, due mostly to repulsion among the adsorbed molecules. The overall heat of adsorption drops to around 10 kcal mol^{-1}. Catalytic reactions are effected at high coverages and these weakly adsorbed molecules are those that participate in the reaction that occurs at high turnover frequency. One surface structure that was obtained (Van Hove *et al.* 1983) at the higher coverage is shown in figure 3*d*. Because of the repulsive interaction the CO molecules no longer occupy only top or bridge sites, but they are relocated in sites of lower symmetry to maximize the distance among them.

Let us consider a catalytic reaction where the desorption of the product molecules is the rate-limiting step. In figure 4 a plot of the turnover rate is presented as a function of the activation energy for the reaction at different temperatures. In obtaining these values, we assume a pre-exponential factor of 10^{12} s^{-1}. Molecules that have desorption activation energies that are less or equal to that represented by the solid line at the given temperature can participate in the catalytic reactions, while those that have higher activation energies are too strongly bound to be able to turn over at the observed rates. Of course, those molecules that are bound so weakly as to have very small activation energies of desorption may not be able to react either, because their surface-residence times are very short. Nevertheless, the surface coverages of weakly adsorbed species may be controlled by the reactant pressure. High pressures

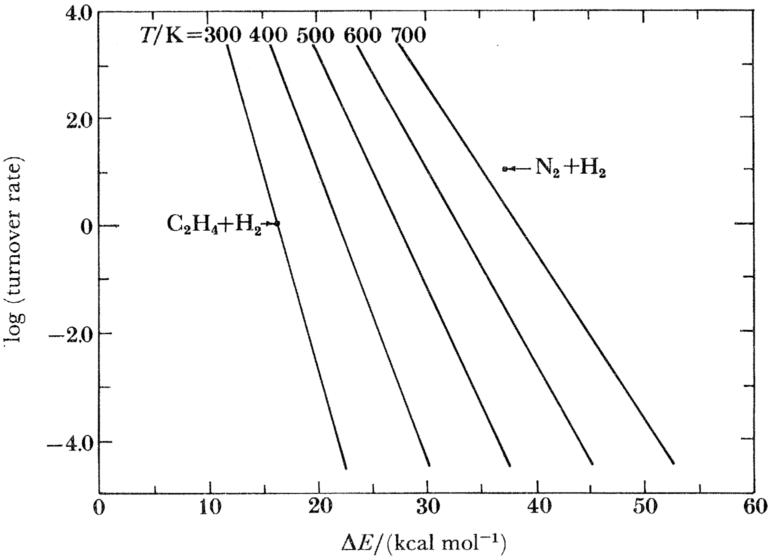


FIGURE 4. The turnover rates as a function of the activation energy for reactions at different temperatures. Pre-exponential factor of 10^{12} s^{-1} is assumed.

favour catalytic reactions that involve weakly bound adsorbates. In figure 4 the turnover rates and reaction activation energies of the hydrogenation of C_2H_4 and the ammonia synthesis are indicated to show two reactions that occur under widely different conditions.

1. Catalytic reactions on metal surfaces

These reactions usually involve strongly adsorbed intermediates and are surface-structure sensitive. Atomically rough surfaces usually exhibit the highest turnover rates. Perhaps the best example of this type of process is the synthesis of ammonia. Figure 5*a* shows the rates over three iron single-crystal surfaces. The (111) orientation crystal face is about 500 times as active as the (110) close-packed surface (Spencer *et al.* 1982). Chemisorption studies by Ertl show equally large differences in the sticking probability of N_2 on these surfaces (Ertl 1981), confirming that the dissociation of N_2 is the rate-limiting step in this reaction. The ammonia synthesis over Re crystal surfaces shows even larger structure sensitivity (Asscher *et al.* 1984) (figure 5*b*); the $(11\bar{2}1)$ and $(11\bar{2}0)$ crystal faces of this h.c.p. metal are over a thousand times as active as the close-packed (0001) crystal face. Figure 5*c* shows the three metal surfaces that are the most active for ammonia synthesis. These surfaces are rough on the atomic scale and have open structures that expose high coordination sites, especially in the second layer. These atoms with large numbers of nearest neighbours are accessible to the incoming N_2 molecules and appear to be most active for dissociation.

Recently, a theory of metal catalysis has been proposed (Falicov & Somorjai 1985) that considers those sites most active in breaking and forming chemical bonds to have a high concentration of degenerate electronic states of low energy, thereby permitting charge fluctuations. There are electronic configurational fluctuations or spin fluctuations that may occur. Electronic configurational fluctuations are the largest at metal sites of high coordination. These are shown for a nickel surface on which six atoms are placed in figure 6. The higher the atomic coordination of the site, the higher the density of electron hole states, n. High coordination sites may be made available in catalytic reactions by using surfaces with open atomic structures so that atoms in the second layer become available to the incoming reactants, or by using stepped and kinked surfaces (Somorjai 1981). The latter surfaces contain in-step atoms of high coordination that are very active in catalytic reactions. Studies of H_2–D_2 exchange (Salmeron *et al.* 1977, 1979), hydrogenolysis (Gillespie *et al.* 1981) and dehydrocyclization reactions over stepped Pt surfaces clearly indicate the higher reactivity of these sites for H–H, C–H or C–C bond breaking.

While the structure sensitivity of many reactions other than ammonia synthesis is well documented by careful catalytic studies, the magnitude of structure-sensitive variations are smaller, by about a factor of 5 or 10, than that for the N_2/H_2 synthesis. More complex reactions require several consecutive reaction steps, some of which are structure sensitive. The need for a more complex catalyst surface in many other reactions will be demonstrated later in this paper. The ammonia synthesis may be viewed as an example of a reaction that obeys Langmuir–Hinshelwood kinetics, which is dominated by the reactions between adsorbed species on the metal surface.

Catalytic reactions that require high coordination metal sites are unique to solid surfaces. Metallo-organic species or clusters frequently used in homogeneous catalysis do not have sufficiently large numbers of metal atoms to produce these high coordination sites. Homogeneous

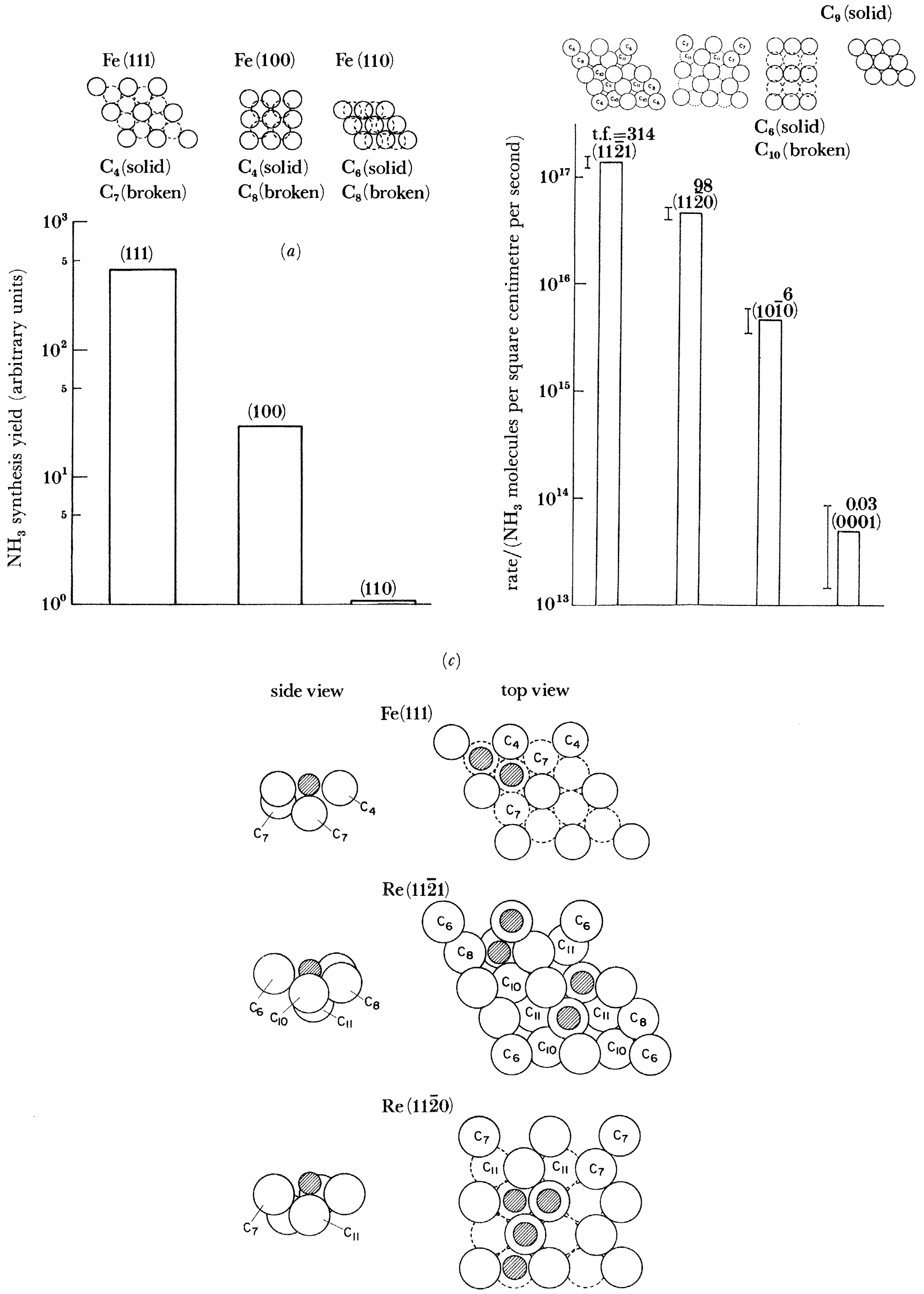
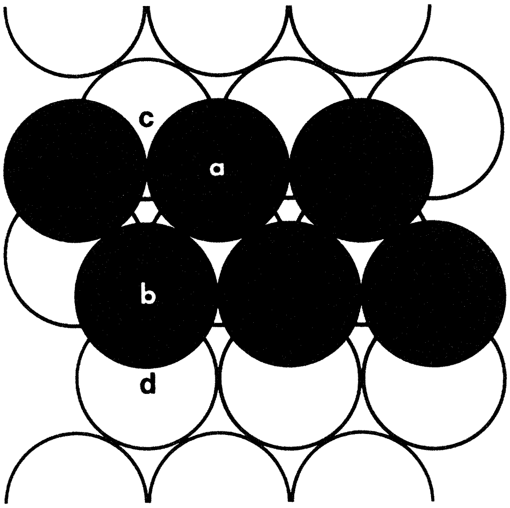


FIGURE 5. The structure sensitivity of catalysed ammonia synthesis on (*a*) iron and (*b*) rhenium single-crystal surfaces: $P_{\text{tot.}} = 20$ atm; $H_2:N_2 = 3:1$; $T_{\text{cryst.}} = 870$ K. C_4, C_6, …, C_n notation indicates the number of nearest neighbours at that atomic site. (*c*) The metal surfaces that are most active for ammonia synthesis.



bulk nickel	$Z(\mathrm{Ni}) = 12$	$n = 0.56$
surface Ni(111) atom	$Z(\mathrm{Ni}) = 9$	$n = 0.38$
outstep nickel atom a	$Z(\mathrm{Ni}) = 7$	$n = 0.25$
outstep nickel atom b	$Z(\mathrm{Ni}) = 7$	$n = 0.24$
instep nickel atom c	$Z(\mathrm{Ni}) = 11$	$n = 0.52$
instep nickel atom d	$Z(\mathrm{Ni}) = 10$	$n = 0.45$
Ni under a Cu(111) monolayer	$Z(\mathrm{Ni}) = 9$ $Z(\mathrm{Cu}) = 3$	$n = 0.52$
Ni monolayer on Cu(111)	$Z(\mathrm{Ni}) = 3$ $Z(\mathrm{Cu}) = 6$	$n = 0.46$

FIGURE 6. A model of the Ni(111) surface with six-atom cluster placed on top of it. The d shell is occupied by 9.44 electrons.

and heterogeneous catalytic reactions may be compared when we consider another class of catalytic reactions next, which occur in the second layer and not directly on the metal surface.

2. CATALYSIS ON TOP OF AN OVERLAYER: THE HYDROGENATION OF ETHYLENE

This simple reaction, which occurs at 300 K or below at atmospheric pressures on many transition metal surfaces, has been the subject of investigations of many researchers including Farkas *et al.* (1934), Eley & Tuck (1936), Beeck (1950), Twigg & Rideal (1939), Schuit (1950), Horiuti & Polanyi (1934), Roberts (1963) and many others (for example Horiuti & Miyahara 1968). I shall restrict my comments to platinum and rhodium, which are among the most active catalysts for this process. Table 3 indicates that the hydrogenation occurs equally well on Pt crystals, films, foils and supported particles, which indicates that the reaction is structure insensitive (Zaera & Somorjai, 1984). When the clean metal surfaces are exposed to ethylene, a strongly adsorbed ordered layer of ethylidyne, C_2H_3, forms. This molecule is shown in figure 7 along with its vibrational spectrum obtained by h.r.e.e.l.s. The kinetics of ethylene hydrogenation and those of ethylidyne have been studied extensively over the (111) faces of Rh and Pt and the rates of these processes are displayed in figure 8. Ethylene hydrogenation occurs at a rate six orders of magnitude higher than the rehydrogenation of the strongly adsorbed ethylidyne. Even the deuteration of the methyl group of ethylidyne occurs very slowly. ^{14}C labelling of the ethylidyne and the vibrational spectroscopy studies confirm these findings (Zaera & Somorjai 1984 and Koel *et al.* 1984).

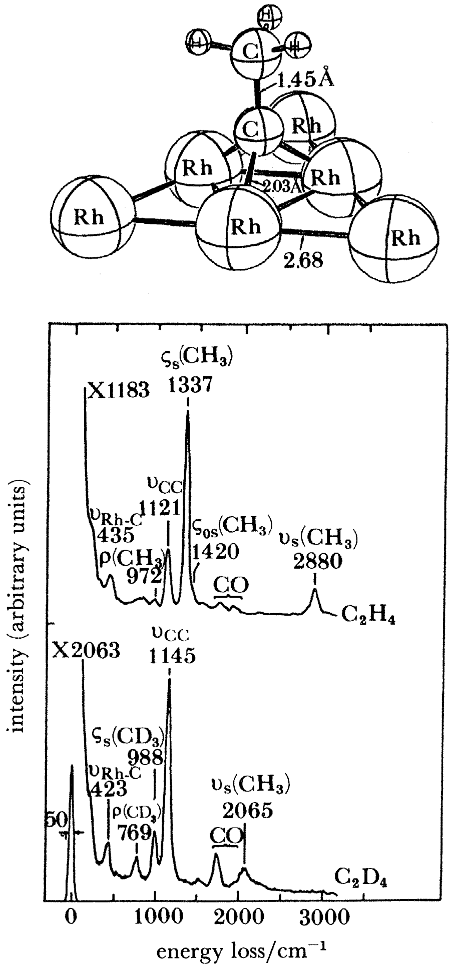


FIGURE 7. Ethylidyne on Rh(111) at 310 K. The stable room-temperature structure of chemisorbed ethylene, its atomic structure and h.r.e.e.l. spectra.

TABLE 3. COMPARISON OF ETHYLENE HYDROGENATION KINETIC PARAMETERS FOR DIFFERENT PLATINUM CATALYSTS

		orders in partial pressures of			
catalyst	log (rate)[a]	ethylene	hydrogen	E_a/(kcal mol^{-1})	reference
platinized foil	1.9	−0.8	1.3	10	Forkes & Forkes (1938)
platinum evaporated film	2.7	0	1.0	10.7	Beeck (1945)
1% (by mass) Pt/Al_2O_3	—	−0.5	1.2	9.9	Bond (1956)
platinum wire	0.6	−0.5	1.2	10	Kazonskii & Struin (1960)
3% by mass Pt/SiO_2	1.0	—	—	10.5	Dorling *et al.* (1969)
0.05% (by mass) Pt/SiO_2	1.0	0	—	9.1	Schlotter & Boudert (1972)
Pt(111)	1.4	−0.6	1.3	10.8	our work

[a] Rate in molecules per platinum atom per second corrected for the following conditions: $T = 323$ K, $P(C_2H_4) = 20$ Torr, $P(H_2) = 100$ Torr.

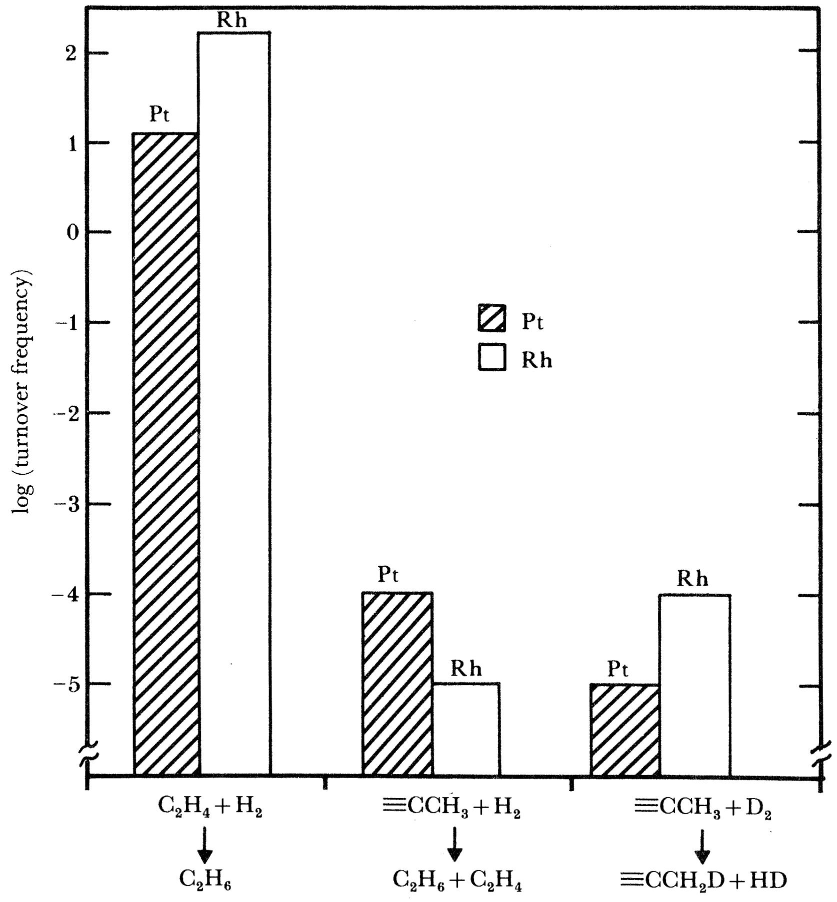


FIGURE 8. The turnover rates for ethylene hydrogenation, the rehydrogenation of ethylidyne, and the deuteration of the methyl group on ethylidyne on platinum and rhodium crystal surfaces at 310 K and 1 atm.

However, the (111) faces of Pt and Rh are covered with a monolayer of ethylidyne during ethylene hydrogenation, since reaction rates are nearly identical over initially clean surfaces and surfaces precovered with ethylene (Zaera & Somorjai 1984 and Beeck 1950). Vibrational spectroscopy studies confirm that the adsorbed monolayer structure on these surfaces after hydrogenation is ethylidyne (Wieckowski *et al.* 1984). So, ethylene hydrogenation occurs rapidly on the C_2H_3-covered surface. The packing of the ethylidyne ordered overlayer does not permit C_2H_4 adsorption directly on the metal surface, as proven by detailed surface science studies with C_2H_4 and C_2D_4. On the other hand, thermal desorption studies show that $H_2(D_2)$ can be dissociatively adsorbed on the ethylidyne-covered metal surface up to about $\frac{1}{4}$ monolayer coverage (Wieckowski *et al.* 1984).

A reaction model that explains these results is shown in figure 9. A hydrogen atom is transferred to the ethylene molecule, which is weakly adsorbed on top of the ethylidyne in the second layer, perhaps by forming an ethylidene intermediate. Such a model of hydrogen transfer from a hydrocarbon to ethylene was first proposed by Thomson & Webb (1976) and our studies corroborate their findings. Our mechanism is of the Eley–Rideal type and is characterized by a low activation energy and structure insensitivity.

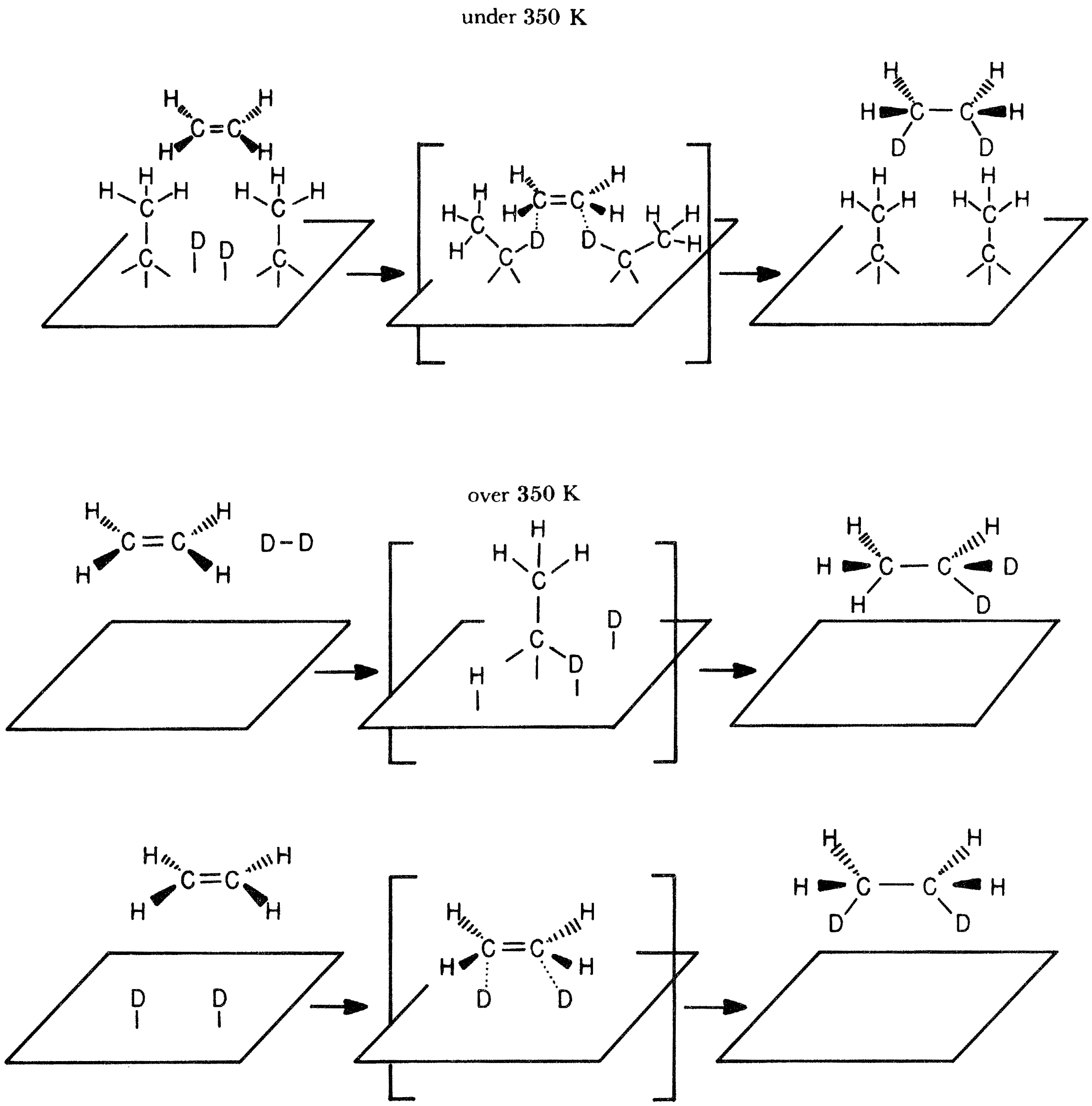


Figure 9. Models of ethylene hydrogenation. Below 350 K the reaction occurs in the presence of a stable ethylidyne monolayer that prevents ethylene adsorption directly on the metal. Above 350 K partial rehydrogenation and removal of the C_2H_3 species frees a fraction of the metal sites, which can now participate in the reaction. In an electrochemical cell or at low temperatures the metal surface may be saturated with atomic hydrogenation before reaction that prevents ethylidyne formation.

However, there are other mechanisms of C_2H_4 hydrogenation that our studies and those of others have uncovered (figure 9). At higher temperatures, the rate of rehydrogenation of C_2H_3 is significant and the bare metal becomes available in part for C_2H_4 hydrogenation. During the electrochemical hydrogenation of C_2H_4 the Pt surface is covered with a layer of hydrogen atoms (hydride) that react rapidly with the approaching C_2H_4 and do not permit the formation of ethylidyne (Wieckowski *et al.* 1985). Thus the complexity of such reactions cannot be underestimated. Nevertheless, it provides an example of reactions of weakly adsorbed molecules in the second layer, an important class of catalytic reactions that could occur at low temperatures or at high pressures. The hydrogenation of CO over certain transition metals that exhibit positive order dependence on both H_2 and CO pressures is thought to occur this way (Logan *et al.* 1984).

These types of reactions may be compared with homogeneous catalytic reactions that are simple, occur at lower temperatures, and include hydrogenation or hydroformylation. Since the metal plays secondary roles in this process, high coordination sites are not needed to effect the reactions. It is hoped that future studies will reveal the possible correlation between homogeneous catalytic reactions and heterogeneous reactions of this type.

3. Reactions over coadsorbate-modified metal surfaces

It appears that most of the catalytic reactions that have been studied so far belong to this class. When two species, atoms or molecules, coadsorb, their chemisorption characteristics are altered. Let us consider the relatively weak interaction of benzene and CO when coadsorbed on Pt and Rh(111) crystal surfaces. Benzene forms a disordered monolayer over Pt in the absence of CO. When CO is introduced several ordered structures form that are detectable by l.e.e.d. (Mate 1985). These structures change, depending on the CO/benzene ratio on the surface, which can be monitored by h.r.e.e.l.s. and t.d.s. Figure 10 shows the various ordered structures that consist of mixed CO–benzene layers with one, two or three CO molecules in the unit cell. The ordering of benzene may be facilitated by the weak attractive interaction with CO that blocks certain alternative adsorption sites. It should be noted that CO is located in a three-fold site (as determined by l.e.e.d. surface crystallography (Van Hove *et al.* 1983) and h.r.e.e.l.s.) that it would never occupy in the absence of benzene. Benzene exhibits a distorted Kekule structure with alternative 1.33 Å† and 1.8 Å bond lengths.

Let us now consider the interaction of coadsorbed sulphur with thiophene, which occurs during the hydrodesulphurization of thiophene on the Mo(100) crystal surface (Gellman *et al.* 1984*b*). This gentle reaction removes the sulphur from the molecule as H_2S in the presence of hydrogen, leaving behind a C_4 species that readily hydrogenates to butadiene, butene and butane without fragmentation. Molybdenum metal strongly adsorbs and decomposes thiophene and butenes, as shown by surface studies, and thus the clean surface cannot be an active catalyst (Gellman *et al.* 1984*a*). MoS_2 is a layer compound and its basal plane holds thiophene so weakly (Salmeron *et al.* 1982) that its thermal desorption occurs at 165 K. So this surface is not chemically active. The active Mo surface contains about one-half monolayer of strongly adsorbed sulphur. These atoms block the metal sites where thiophene decomposition would occur. ^{35}S labelling studies indicate that these sulphur atoms remain permanently on the metal surface during the catalytic reactions. The sulphur atom that is removed from the thiophene occupies sites of weaker bonding where hydrogenation to H_2S and subsequent desorption occurs, while the C_4 species partly hydrogenate also and desorb (Gellman & Somorjai 1985). Thus the blockage of certain adsorption sites on the surface of early transition metals attenuates their strong bonding and permits the catalytic reaction to occur.

Potassium is frequently used as a promoter in many catalytic reactions. The hydrogenation of CO and the synthesis of NH_3 are perhaps the best known examples of potassium promotion. Potassium has a very high heat of adsorption at low coverages (*ca.* 60 kcal mol^{-1}) on most transition metal surfaces, which indicates complete ionization of the atom (Garfunkel 1982). At higher coverages, however, mutual depolarization of the charged potassium species leads

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

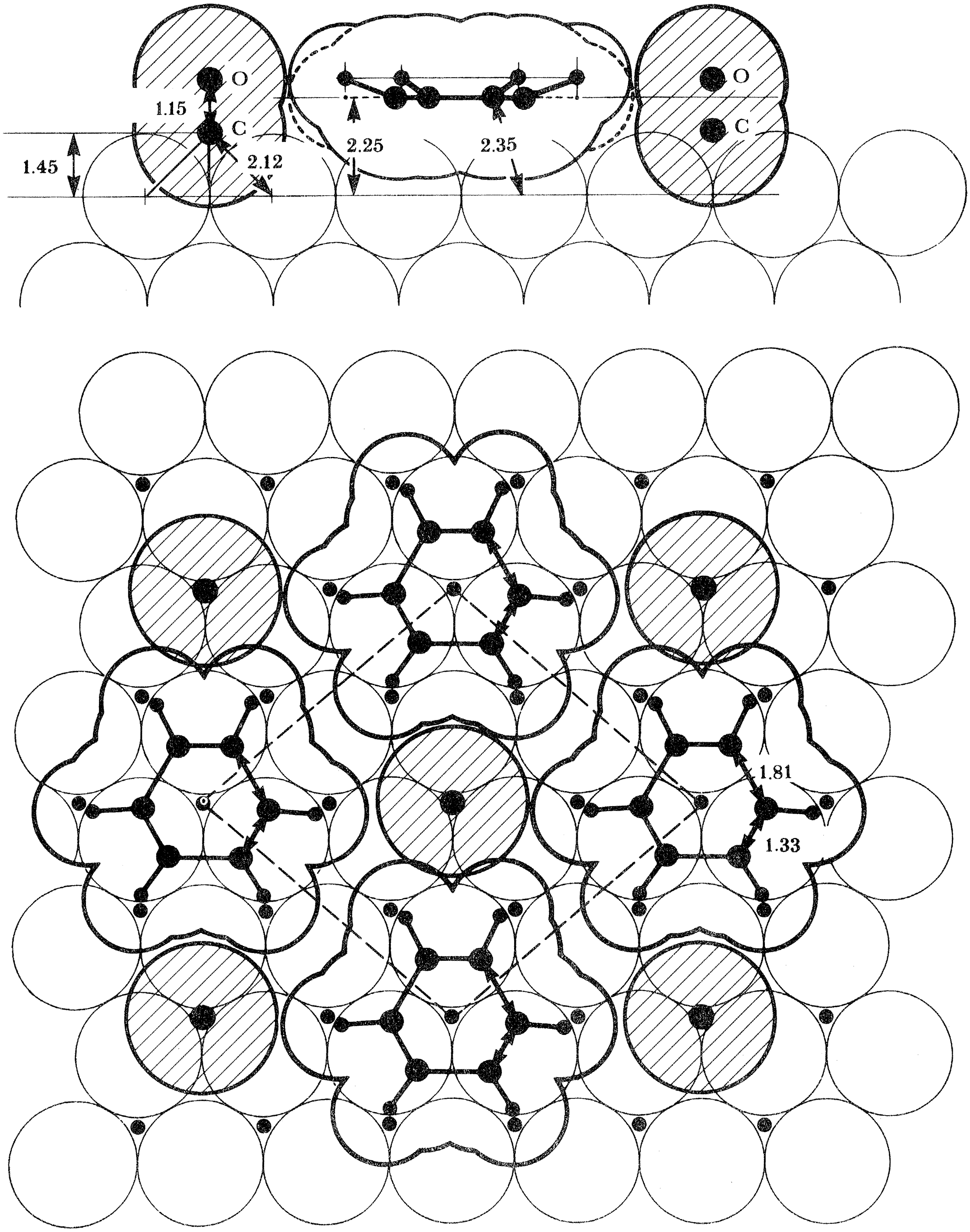

Figure 10. An ordered surface structure composed of carbon monoxide and benzene in the same unit cell. All dimensions are in ångströms.

to neutralization. When *ca.* 50% coverage is reached the heat of adsorption equals the heat of sublimation of metallic potassium (*ca.* 23 kcal mol^{-1}), indicating that the adsorbed atoms are no longer ionized.

The coadsorption of potassium with CO leads to the strengthening of the M–C bond by over 11 kcal mol^{-1} and the simultaneous weakening of the C=O bond, as shown by temperature-programmed desorption and h.r.e.e.l.s. studies, respectively (Garfunkel *et al.* 1983 and Crowell *et al.* 1982). This is because the charge that is transferred from the potassium to the transition metal finds it way into the molecular orbitals, both bonding and antibonding, of CO. On the clean Rh(111) surface, CO stays molecularly adsorbed at low pressures while it dissociates near its desorption temperature in the presence of potassium (Crowell *et al.* 1985). This can be studied by the adsorption of a mixture of $^{12}C^{18}O$ and $^{13}C^{16}O$ and detecting $^{13}C^{18}O$, the product of scrambling, which clearly identifies that dissociation of molecular CO occurred. In figure 11 we show that three CO molecules may dissociate per potassium atom at a potassium coverage where maximum charge transfer to the transition metal occurs. Thus potassium exerts a strong electronic influence that alters the bonding of CO and of hydrocarbons or N_2, as has been studied extensively and demonstrated.

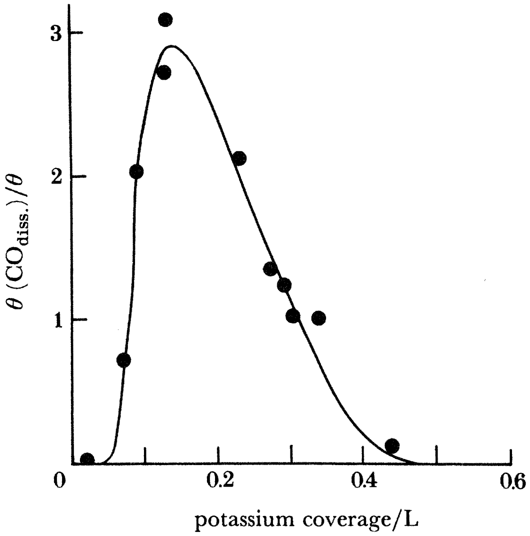

FIGURE 11. The amount of dissociated carbon monoxide per potassium atom as a function of potassium coverage on the Rh(111) single-crystal surface.

The catalytic properties of transition metals may also be altered by alloying with another metal that may be considered a coadsorbate as well. For example, the addition of gold to Pt markedly changes the catalytic selectivity during the reaction of *n*-hexane. This is shown in figure 12*a*, when gold is deposited on the Pt(111) crystal face and then alloyed by heat treatment. Its presence greatly enhances the rate of isomerization, while it simultaneously reduces the hydrogenolysis and dehydrocyclization rates. This effect on the reaction selectivity was attributed to preferential removal of high coordination threefold sites by gold substitution. These Pt sites are responsible for the hydrogenolysis and dehydrocyclization reactions, while isomerization occurs at bridge sites that are not much affected by the presence of gold. However, the effect of alloying is also surface-structure sensitive (Yeates & Somorjai 1985), as shown in figure 12*b*. When a Pt(100) crystal face is used, the change of catalytic selectivity is not observed. All reaction rates decline in proportion to the presence of the inactive gold on the Pt surface.

Finally, we should consider the ever present strongly adsorbed carbonaceous deposit as a coadsorbate that alters the catalytic behaviour of the transition metal. The alkylidyne species that are often present at 300 K or below on transition metal surfaces dehydrogenate sequentially (Salmeron & Somorjai 1982) as the temperature is increased. Depending on the transition metal, either C–H or simultaneous C–H and C–C bond breaking may occur to leave behind carbonaceous fragments that are readily detectable by h.r.e.e.l.s. (Koestner *et al.* 1983). Some of these are shown in figure 13. CH, C_2, C_2H, CH_2 and C_2H_3 fragments have been identified (Davis 1982 and Minot *et al.* 1982), although they undergo polymerization at higher temperatures and finally a graphite or carbide layer that contains no hydrogen will form. The presence of the carbonaceous fragments is essential on many metal catalyst surfaces since these fragments readily transfer hydrogen as long as they contain a large concentration of C–H bonds. The catalyst surface deactivates upon graphitization of this carbonaceous overlayer. The working Pt catalyst for hydrocarbon conversion reactions requires both bare metal sites of appropriate structure and the presence of a hydrogen-transferring carbonaceous overlayer, which adsorbs reaction intermediates only weakly, to attain optimum catalytic activity and selectivity. In addition, active kink sites, which would effect the undesirable hydrogenolysis reaction, could be blocked by strongly adsorbed sulphur. Reaction selectivity is further enhanced by the presence of a second component metal for selective metal catalysis. Thus the active and selective catalyst is a complex system indeed, but it is also within our ability to understand and control.

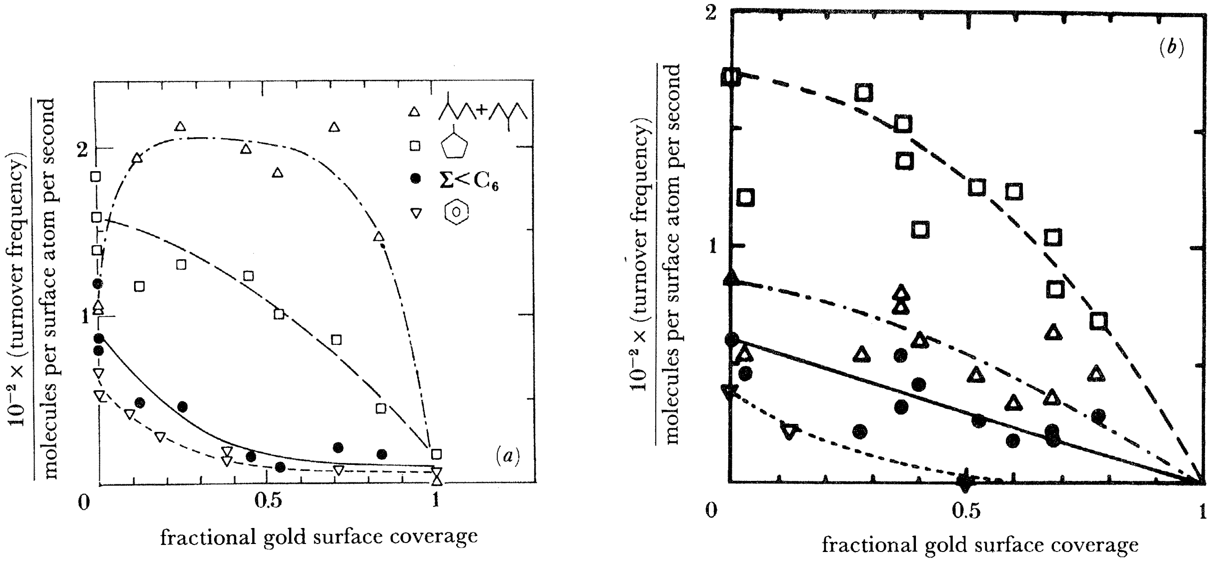

FIGURE 12. The rates of formation of various products from *n*-hexane conversion as a function of fractional gold-coverage for gold–platinum alloys that were prepared by vapourizing gold onto (*a*) Pt(111) (566 K, 220 Torr) and (*b*) Pt(100) (573 K, 220 Torr) crystal surfaces, respectively.

It might be worthwhile to summarize the essential contributions of modern surface science

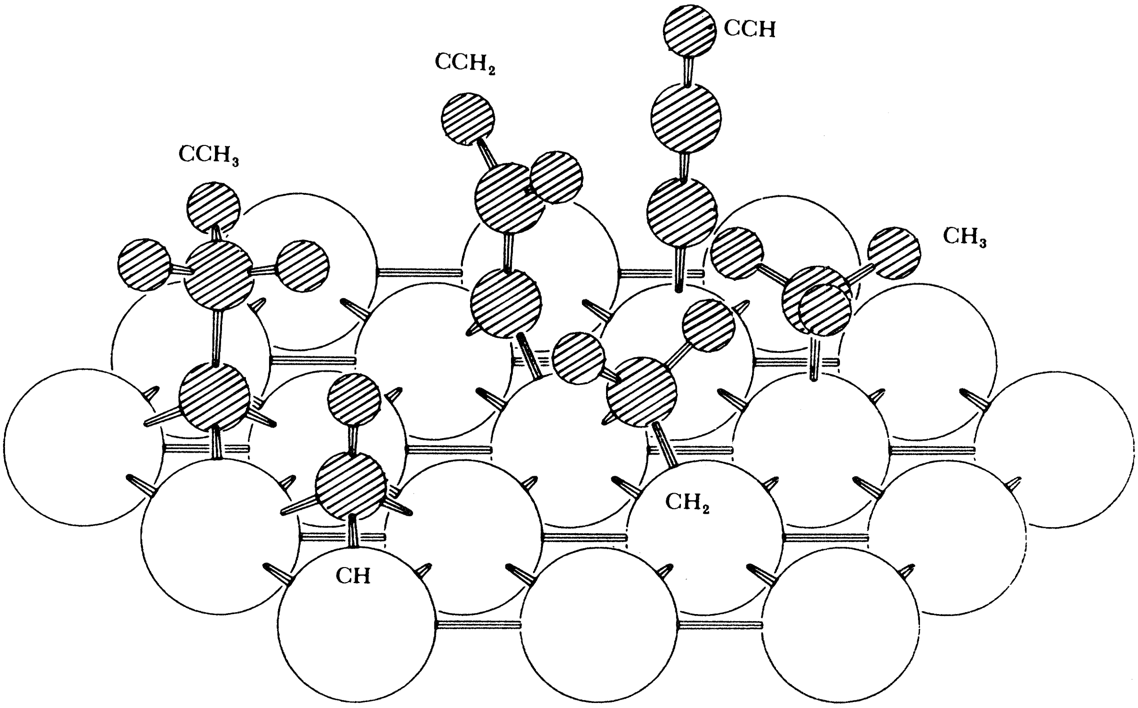

FIGURE 13. Schematic representation of the various organic fragments that are present on metal surfaces at high temperature. The presence of CH, C_2, C_2H, CH_2 and CCH_3 species have been detected.

to heterogeneous catalysis. It has contributed new methods for catalyst characterization on the atomic scale and it has elucidated the roles of surface structure and of coadsorbates of many types. As a result, a molecular view of heterogeneous catalysis has emerged.

There are many opportunities for research in catalysis science that could open up new directions for technology as well. Among them are the need to develop time-resolved techniques for the detection of short-lived species on the surface. It appears that catalysis at low temperatures around 300 K and in aqueous phase is being used by nature successfully, but has not received the attention of catalytic researchers that it deserves. The catalysis of molecules in their excited states is another area of research opportunities in catalysis science.

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Discussion

M. W. Roberts (*Department of Chemistry, University College, Cardiff, U.K.*). Professor Somorjai raised the question of predicting the outcome of a molecule–surface interaction. I would like to illustrate the severity of the problem with which we are faced by drawing attention to the influence of gas *pressure* on the surface chemistry. Dichlorine at Ni(100) generates a $c(2\times 2)$ l.e.e.d. pattern, and if this adlayer is now exposed to dichlorine at 10^{-3} Torr, i.e. an increase in increasing the pressure by a factor of about 10^4, a molecular dichlorine overlayer is generated. This is estimated to be about 15 Å thick. The unusual feature of this overlayer is that it is thermally stable and is characterized by a discrete feature in the valence photoelectron spectrum at about 2 eV below the Fermi level. We suggest this peak reflects a hybridized state generated from the Cl, 3s, 3p and 3d orbitals analogous to bonding in the interhalogens. What is puzzling is the specific and special role played by the Ni(100) $c(2 \times 2)$–Cl structure in stabilizing the molecular overlayer.

J. M. Thomas (*Department of Physical Chemistry, University of Cambridge, U.K.*). Professor Somorjai has raised the important question of how we should set about tackling surface studies with techniques that possess greater spatial and temporal resolution than those now in common use.

Later, my colleagues and I (Thomas *et al.*, this symposium), and others (for example, Venables *et al.*, this symposium) will discuss how electron microscopic procedures can make significant contributions in this regard. Electron microscopes can, these days, be made to function as versatile 'chemical laboratories' where diffraction, spectroscopy and imaging can all be undertaken in sequence or in parallel. Diffraction serves to identify the phase and to convey (from the degree of diffuse scattering or streaking) the degree of order within that phase. On Fourier transforming the diffraction pattern, which is what the objective lens does, an image is produced. Such is the measure of high resolution attainable in modern microscopes that the images now achievable have a spatial resolution of better than 2.5 Å. This is enough to identify the junctions between a metal (or a metal silicide) and silicon, of the type alluded to by Professor Siegbahn earlier. Likewise, high-resolution images taken along the appropriate zone axis (Thomas & Millward 1982), can reveal microstructural intergrowths, at the sub-unit all level, in crystalline high-area catalysts such as ZSM-5 and ZSM-11.

Moreover, by adding a solid state detector and an electron spectrometer to the microscope one may obtain, respectively, an electron-induced X-ray emission spectrum (and hence the elemental composition) and several different kinds of electron spectroscopic information, which we shall describe more fully in our own paper. Such spectroscopic information is extracted under exceptionally favourable conditions of spatial resolution (particles of *ca.* 100 Å diameter and sample masses of less than 10^{-16} g). Particularly useful is the fact that, for transition metal oxides the number of d electrons can be deduced from the magnitude of the 'white-line' electron energy loss 'edge' spectra.

So far as improvements in temporal resolution are concerned, neutron scattering techniques have considerable promise (see discussion comment after Roberts's paper, this symposium).

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N. Sheppard (*School of Chemical Sciences, University of East Anglia, U.K.*). Professor Somorjai has given excellent molecular details to illuminate the concept that the hydrogenation of ethylene on a metal surface involves a 'carbonaceous' layer. Has he a similar scheme in mind related to another structural insensitive reaction, the hydrogenation of benzene (or the dehydrogenation of cyclohexane)?

G. A. Somorjai. I would like to think that other structure-insensitive hydrogenation reactions may also have mechanisms similar to that of ethylene hydrogenation at 300 K over rhodium and platinum. However, benzene hydrogenation is usually performed at higher reaction temperatures where the metal surface is likely to be partly covered with carbonaceous fragments, CH and C_2H, as indicated by high-resolution electron energy loss spectroscopy studies. At these higher reaction temperatures, dictated by the higher activation energies for the reaction, the rates of rehydrogenation of the strongly adsorbed fragments are also higher, which open up bare metal surface sites. It is therefore likely that benzene hydrogenation may partly occur over the carbonaceous fragments and in part over the bare metal catalysts. Unfortunately combined catalytic and surface science studies are not yet available for this reaction.

The dehydrogenation of cyclohexane appears to be structure sensitive (Herz *et al.* 1981).

Reference

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J. M. Thomas (*Department of Physical Chemistry, University of Cambridge, U.K.*). I was intrigued to observe the bond distance exhibited by the benzene molecule coadsorbed with carbon monoxide on the rhodium surface. The single bond length that Professor Somorjai quotes (1.81 Å) exceeds by a substantial margin what I believe to be the longest recorded single bond length known hitherto (in di-anthracene). Are we really dealing with the Kekule benzene here or could it be three acetylene molecules on Rh(111)?

G. A. Somorjai. It appears that we have distorted benzene molecules on both Rh(111) and Pt(111) crystal surfaces. High-resolution electron energy loss spectroscopy measurements show clearly the presence of C–C breathing modes at 1330 $\mathrm{cm^{-1}}$ and at 1430 $\mathrm{cm^{-1}}$, which are not present for adsorbed acetylene on these crystal faces (Mate & Somorjai 1985; Ibach & Lehwald 1978). L.e.e.d. surface structure analysis indicates that benzene lies with its π-ring parallel to both metal surfaces centred over a three-fold hollow site on Rh(111) and a bridge site over Pt(111), with alternating C–C bond distances of 1.8 ± 0.15 Å and 1.33 ± 0.15 Å over rhodium. Long C–C bond distances have been measured in a number of molecules. The longest distance we are aware of is 1.85 Å in a bisnorcaradiene, related to [10]-annulene (Bianchi *et al.* 1978).

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