THE REACTIVITY OF ORDERED METAL LAYERS ON SINGLE CRYSTAL SURFACES OF OTHER METALS: Au ON Pt(100) AND Pt ON Au(100)

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Gold was deposited on Pt(100) and platinum was deposited onto a Au(100) single crystal surface. The variation of the reactivity of these surfaces with coverage of the adsorbate metal was studied using the cyclohexene dehydrogenation to benzene as a test reaction. The reactions were carried out with 6×10^{-8} Torr (8.0×10^{-6} Pa) cyclohexene in hydrogen with a partial pressure of 1×10^{-6} Torr (1.3×10^{-4} Pa) at 373 K It was found that the reactivity of a Pt(100) surface is enhanced about six-fold by the deposition of just one monolayer of gold that itself is not measurably active under these reaction conditions. When the gold coverage exceeds one monolayer the reactivity decreases. The deposition of platinum onto a Au(100) single crystal surface causes an increase in the reactivity until a broad maximum is reached at about 1.5–2 layers of platinum. At this maximum the reactivity is six times larger than that of a Pt(100) single crystal surface. Beyond three to four layers, the reactivity decreases slowly with increasing platinum coverage and approaches the reactivity of the clean Pt(100) single crystal surface.

1. Introduction

In recent years alloys of transition metals have been used increasingly as catalysts in the chemical technology. These alloys are of special importance in the catalysis of hydrocarbon reactions for several reasons. On the one hand they are more selective in forming certain products. On the other hand, they have a higher resistance to deactivation that permits their use at higher temperatures where they remain stable while carrying out catalytic reactions at higher rates and with a better selectivity than the one-component metal catalyst systems. Pt–Ir [1,2], Pt–Re [3–8], Pt–Sn [9], Pt–Au [10–13], and Ni–Cu [14–16] alloys, systems are examples of such catalysts. Sinfelt studied in some detail the activity of several alloy systems as a function of composition and proved the existence of bimetallic clusters that have unique thermodynamic properties (miscibility) [17] and struc-

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ture (raft-like) [18]. Theoretical scrutiny of these clusters has been undertaken by Falicov et al. [19,20]

In studies of small alloy particles that are supported on high surface area oxides it is difficult to control the surface structure and composition independently. In order to understand the reasons for the altered chemical behavior of these alloy particles it is important to be able to vary the surface composition while retaining the same surface structure in order to separate these important experimental variables.

For this reason we undertook a study of metal layers that were epitaxially deposited on ordered single crystal surfaces of other metals. In particular we report the reactivity of the gold—platinum system. In a series of experiments, gold was deposited from the vapor phase onto a Pt(100) single crystal surface in amounts ranging from a fraction of a monolayer to several layers. Then the rate of dehydrogenation of cyclohexene to benzene was monitored as a function of gold coverage. Conversely, platinum was deposited from the vapor phase onto a Au(100) single crystal surface in submonolayer-to-multilayer amounts, and the reactivity for the same dehydrogenation reaction was measured as a function of platinum coverage. The detailed investigation of the structure of these metal films (Au on Pt(100) and Pt on Au(100)) is reported in a separate paper [21].

We have found that the rate of benzene formation increases about four-fold (six-fold after correction for the edges of the Pt(100) single crystal that remain uncovered during gold deposition) following the deposition of one monolayer of gold on Pt(100) as compared with the rate on the pure Pt(100) single crystal. When the monolayer gold coverage is exceeded, the rate decreases. The rate of cyclohexene dehydrogenation is also enhanced upon the deposition of platinum onto the Au(100) single crystal surface. Initially, the rate of benzene formation increases with platinum coverage until a broad maximum is reached at about 1.5—2 layers. Beyond 3 to 4 layers the reactivity decreases slowly with increasing platinum coverage. The reaction rate at the maximum is 3 to 4 times higher than that on a Pt(100) single crystal. If the reactivity of the latter is corrected for contribution of the edges, an enhancement of a factor of about 6 results.

2. Experimental procedures

The experiments were carried out in an ultrahigh vacuum (UHV) system under low pressure flow conditions. Hydrogen and cyclohexene were continuously introduced through separate leak valves, and the gas mixture was pumped by a conductance-limited diffusion pump. The quadrupole mass spectrometer that was used to monitor the reaction rates was calibrated against a nude ion gauge. The surfaces were prepared by vapor deposition of the adsorbate metal onto the clean substrate surface. When platinum was used as a substrate, the front and back (100) faces were covered with equal amounts of gold. The Au(100) single crystal was covered with

platinum only on one side. Details of the preparation and characterization of the surfaces by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) are described in a separate paper [21].

Briefly, it was found that platinum deposited onto the Au(100) single crystal surface grows via the formation of microcrystallites (Volmer–Weber type growth), while gold on Pt(100) grows layer-by-layer (Frank–van der Merwe growth). For this reason the platinum coverages will be expressed in monolayer equivalents which are defined as the ratio of the total number of deposited atoms to the number of surface atoms. In the case of a layer-by-layer growth mechanism the number of monolayer equivalents is identical to the number of monolayers. In this paper the term "layer" is used also in the sense of monolayer equivalents.

The cyclohexene dehydrogenation reaction was carried out at a cyclohexene partial pressure of 6×10^{-8} Torr (8.0×10^{-6} Pa) in excess hydrogen of 1×10^{-6} Torr (1.3×10^{-4} Pa) at 373 K. The hydrogen used in these experiments was 99.999% pure, the cyclohexene 99.5$^+$ mole%. The cyclohexene was purified of dissolved gases by repeated freeze-pump-thaw cycles.

Since the entire vacuum chamber was exposed to the gas mixture, the reaction also occurred on the chamber walls to some extent. It was not possible to prevent deposition of some platinum onto the chamber walls when cleaning the Pt(100) single crystal by argon ion bombardment, or when evaporating platinum onto the Au(100) substrate. In the latter case, the contamination of the chamber walls with active metal was minimized in two ways. First, the evaporation source was placed in a differentially pumped second chamber that was connected to the main chamber only by a small collimating hole. Second, a gold foil was placed behind the substrate single crystal in order to adsorb the evaporated platinum atoms that did not impinge on the crystal (the beam of evaporated metal had a cross section that was larger than that of the substrate single crystal to ensure homogeneous deposition over the entire surface). Subsequent resistive heating of this foil then caused the platinum to diffuse into the bulk of the gold foil, rendering it inactive during subsequent reaction studies. Still, the background reactivity due to the chamber walls was not negligible and varied in magnitude from experiment to experiment.

The following procedure was used to determine both the reactivity of the single crystal and the background reactivity in the same experiment. After preparation and characterization of the surface, the reactant gases were introduced and the reaction was monitored for about 30 min with the crystal at 300 K. Then the crystal was heated to the reaction temperature of 373 K. After measuring the reaction rate at this temperature for about an hour, the experiment was continued for an additional half hour while cooling the crystal to room temperature. The background reactivity was then obtained by interpolation between the two sets of data taken before and after the reaction at 373 K and subtracted. The reaction rates were corrected for the cyclohexene pressure drop during reaction using the first order dependence of the rate on cyclohexene pressure [22]. In order to calculate specific rates, expressed as turnover frequencies (molecules per surface atom per second),

the number of surface atoms of the single crystal is needed. This was easily obtained by multiplying the geometric surface area of the single crystal with the concentration of atoms per unit area that can be calculated from available crystallographic data on platinum and gold [23] (1.30×10^{15} and 1.20×10^{15} atoms/cm^2, respectively, for the (100) crystal face).

3. Experimental results

3.1. Cyclohexene dehydrogenation to benzene

A typical variation of the rate of cyclohexene dehydrogenation to benzene with time is shown in fig. 1. As described in the preceding section, the reaction at 373 K was preceeded and followed by measurements with the crystal at room temperature. The reaction rate shows a sharp increase when the crystal is heated to the reaction temperature, reaches a maximum value after several minutes, and decreases thereafter. The induction time before the maximum is reached is always longer than the time needed for the crystal to reach the reaction temperatures of 373 K. Self-poisoning was found in all cases, gold on Pt(100), platinum on Au(100), and also pure Pt(100). Qualitatively the behavior of all these systems is the same, quantita-
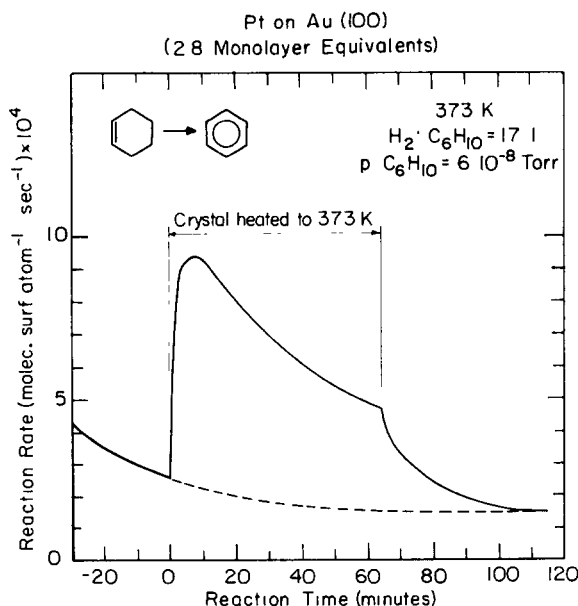

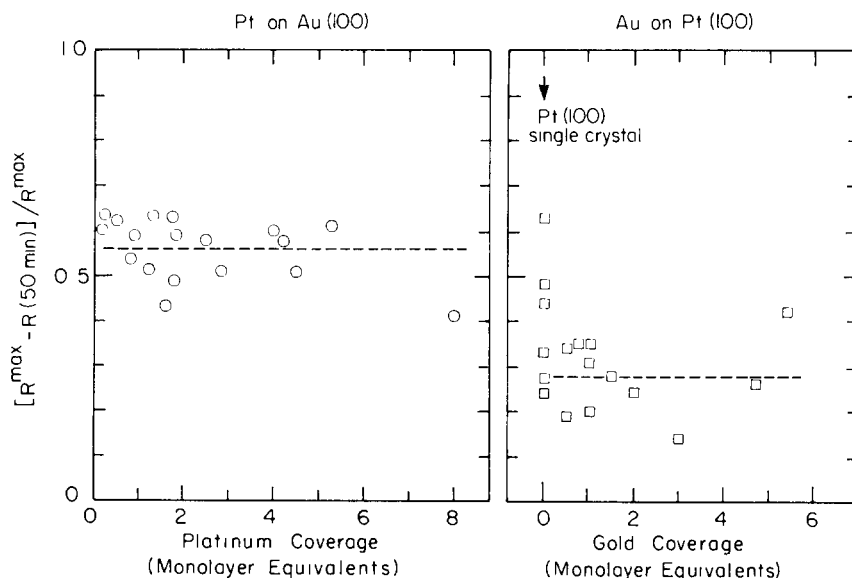Fig 1. Typical variation of the rate of cyclohexene dehydrogenation to benzene with reaction time.

Fig. 2. The normalized decline of the reaction rate $[R^{max} - R(50\ min)]/R^{max}$ that is taken as equal to the self-poisoning rate, plotted as a function of the adsorbate metal coverage.

tively the rate of self-poisoning is higher for platinum on Au(100) than for gold on Pt(100). The rates of self-poisoning on a Pt(100) single crystal surface found in different experiments show some scatter and vary between these two sets of values. This is illustrated in fig. 2, where the difference between the maximum reaction rate and the rate after 50 min reaction time, divided by the maximum reaction rate ($[R^{max} - R(50\ min)]/R^{max}$) is taken as equal to the rate of self-poisoning.

It should be emphasized that, as fig. 2 shows, both for the Au on Pt(100) and Pt on Au(100) systems, the rate of self-poisoning is independent of the adsorbate metal coverage. Also, the induction time, which varies from 3 to 16 min for the Au on Pt(100) system, and from 2 to 7 min for the Pt on Au(100) system does not depend on the adsorbate metal coverage.

Because of the adsorbate metal coverage independence of the induction time and the self-poisoning, the maximum reaction rate can be used as a simple parameter to characterize the reactivity of a surface. It is this maximum of the reaction rate with time that is plotted in figs. 3 and 4 as a function of the adsorbate metal coverages. These data are described in detail in the following sections.

The dehydrogenation of cyclohexene was carried out in excess hydrogen to enable comparison with previous work on this reaction that was carried out in this laboratory [24]. However, an experiment carried out in the absence of hydrogen gave the same result as the corresponding experiment with hydrogen. Also, replacing the hydrogen by deuterium did not cause any changes in the reactivity or
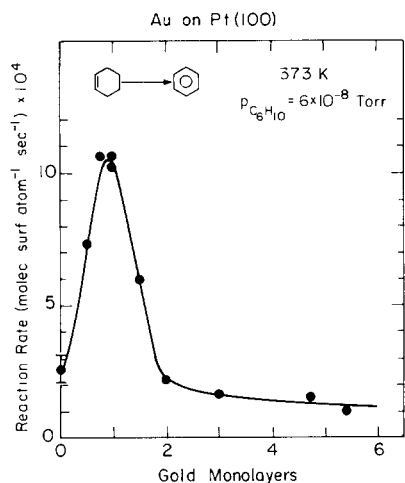
Au on Pt (100)

Fig 3. Variation of the rate of cyclohexene dehydrogenation to benzene with Au coverage on Pt(100)

self-poisoning behavior, not did it result in the formation of deuterated cyclo-hexene or benzene, indicating that the added gas phase hydrogen actually does not participate in this reaction. Under our reaction conditions, cyclohexene solely underwent dehydrogenation to benzene.
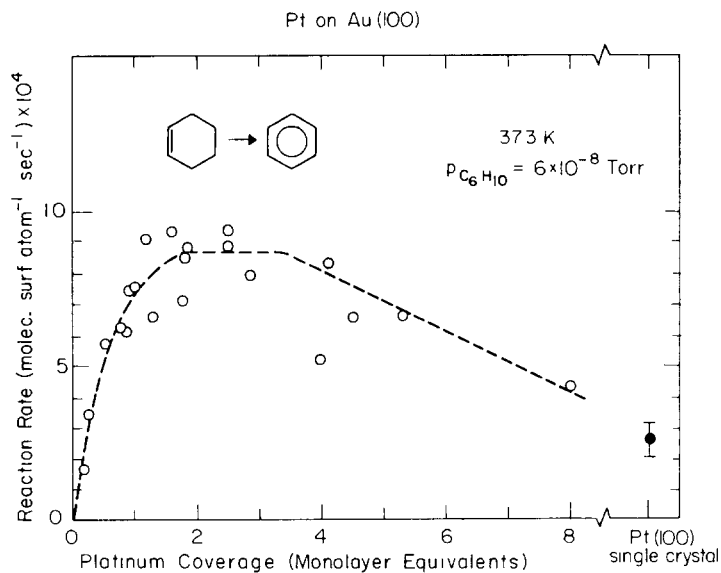
Pt on Au (100)

Fig 4. Variation of the rate of cyclohexene dehydrogenation to benzene with Pt coverage on Au(100).

3.2. The reactivity of the gold on Pt(100) system

The variation of the reactivity of a Pt(100) single crystal surface with gold coverage is shown in fig. 3. A striking increase in reactivity is observed when gold, itself not measurably active for this reaction, is deposited onto a Pt(100) single crystal surface. At the monolayer coverage the reactivity reaches a maximum, at which point it is enhanced by a factor of 4 relative to the specific rate on the pure Pt(100) single crystal. The measured value of the reactivity does, however, include the contribution from the edges of the crystal. Since the edges do not get covered by gold during the deposition onto the front and back faces of the platinum crystal, their contribution which is found as the tailing value of the curve in fig. 3 at high gold coverages, should be subtracted from all reactivities reported in fig. 3. Taking this into account, the enhancement of the reactivity of a Pt(100) surface by a monolayer of gold is actually about 6-fold. When the gold coverage exceeds the monolayer the reactivity decreases rapidly and reaches the low level that is due to the edges of the platinum single crystal.

It should be emphasized that in the calculation of the reaction rates, which are specific rates or turnover frequencies, it has not been taken into account that the number of surface platinum atoms decreases with increasing gold coverage. Instead, the reaction rates have all been calculated using a constant number of surface atoms, i.e. the number of platinum atoms on the clean Pt(100) single crystal surface. Otherwise, the reaction rates would approach infinity as the number of surface platinum atoms vanishes at the completion of the gold monolayer.

AES shows that after reaction the pure Pt(100) surface is covered by about one-half monolayer of carbon. A peak ratio of the carbon 272 eV and platinum 237 eV Auger transitions of 3.2 was used to identify one carbon monolayer [25], which corresponds to an absolute coverage of 2 carbon atoms per surface atom [26]. As gold is deposited onto the platinum, the amount of carbon that is deposited by the reaction decreases and vanishes at the monolayer gold coverage.

At gold coverages of one monolayer or more, AES shows no difference between the surface before and after reaction. However, the surface has been poisoned irreversibly by the reaction. An attempt to restore the reactivity of a surface after reaction by flashing it to 735 K in vacuum was unsuccessful. About 60% of the original activity of a Pt(100) covered with one monolayer of gold could be restored by treating the surface, after reaction, in oxygen (675 K, 5×10^{-7} Torr (6.7×10^{-5} Pa) O_2, 5 min). In order to investigate the nature of the reaction self-poisoning the following two experiments were carried out where a freshly prepared Pt(100) surface covered with a gold monolayer was "aged" prior to the reaction. One treatment consisted of heating the crystal to 373 K in vacuum for one hour, the other of heating the crystal to 373 K in vacuum for one hour in the presence of 1×10^{-6} Torr (1.3×10^{-4} Pa) hydrogen. The reactivity of the surfaces following these treatments retained its high value in both cases.

3.3. The reactivity of the platinum on Au(100) system

Fig. 4 shows the reactivities of the Au(100) single crystal surface covered by varying amounts of platinum. In this system also an enhancement of the reactivity with respect to a pure Pt(100) single crystal surface is found. The reactivity increases initially with platinum coverage, reaching a broad maximum or plateau after 1.5 to 2 monolayer equivalents (mle). When the platinum coverage exceeds 3 to 4 mle the reactivity decreases slowly. At the maximum, the reactivity of the surface is enhanced by a factor of 3 to 4 relative to the pure Pt(100) single crystal. When the latter value is corrected for the contribution from the crystal edges, the enhancement of the reactivity is found to be about 6-fold. Also in this system all reaction rates have been calculated using a constant number of surface atoms, i.e the number of surface atoms of one face of the Au(100) single crystal. The actual number of platinum surface atoms in the platinum on Au(100) is not known due to the lack of accurate information on the platinum crystallite sizes and shapes.

One complication in the case of the Pt on Au(100) system is the occurrence of some carbon contamination of the surface during the deposition of platinum, since platinum could only be deposited at rather low rates. The amount of carbon present before the reaction was about 4% of the amount of deposited platinum. The reactivities that are reported in fig. 4 have been corrected for the surface area blocked by the carbon using the AES calibration for carbon on platinum by Biberian et al. [25]. However, this correction did not change any of the important features of the curve in fig. 4, and changes the maximum value of the reactivity only by about 10%.

During the reaction, carbon would be deposited on the surface. The amount of carbon present after reaction increases initially with platinum coverage until it saturates at the value for the bulk Pt(100) single crystal surface at a platinum coverage of about 3 mle.

4. Discussion

4.1. The cyclohexene dehydrogenation reaction

At present the mechanism of the low pressure cyclohexene dehydrogenation to benzene is not well understood. The reaction rate increases when the crystal is heated to the reaction temperature, but the increase still continues after this temperature has been reached. After several minutes the rate reaches a maximum value and decreases thereafter due to self-poisoning. The decrease of the reaction rate with time is more or less exponential indicating that it is a first-order process in the number of remaining active sites. The rate of self-poisoning is higher for Pt on Au(100) than for Au on Pt(100), but does not depend on the adsorbate metal coverages for these systems. On the contrary, the rates of benzene formation

depend strongly on the platinum and gold coverages, respectively. This implies that benzene formation and self-poisoning are parallel and independent reactions. AES spectra taken of the surfaces before and after the reaction showed no detectable exchange between platinum and gold atoms in either of the two systems; the reaction temperature was chosen as low as 373 K for just this reason. Also LEED gave no evidence for reaction-induced restructuring of the surface. Aging of a Pt(100) surface covered by a monolayer of gold in vacuum or in 1×10^{-6} Torr (1.3×10^{-4} Pa) hydrogen did not reduce the reactivity measured during the subsequent experiments. Consequently, the self-poisoning is due to the presence of adsorbed cyclohexene.

Using AES it was observed that the reaction deposited some form of surface carbon on those surfaces where platinum was present in the outermost layer. This carbon could certainly block sites, rendering the surface inactive. However, in the Au on Pt(100) system it was found that the amount of carbon present after reaction would decrease with increasing gold coverage and vanish at coverages of one monolayer of gold without changing the poisoning behavior. This might be rationalized in two ways. On the one hand it may be that the reaction actually occurs at defect sites, i.e. platinum atoms that have not been covered by gold. A small concentration of defect sites would not have been detected in the LEED and Auger characterization of this system [21]. These defect sites poison in the same way as clean platinum, but since their concentration is very small the surface coverage of the carbon that is deposited would be smaller than the detection limit of AES, i.e. smaller than about 3% of a monolayer. On the other hand, if one accepts the absence of surface carbon after reaction, it then seems that the self-poisoning should be related to the hydrogen that is abstracted from the cyclohexene during the dehydrogenation reaction. Accumulation of hydrogen at the surface should indeed inhibit the dehydrogenation. The presence or the nature of a hydrogen species at the surface cannot be studied by AES, however. It is puzzling that if hydrogen accumulation at the surface is the cause for the self-poisoning, flashing a surface of Pt(100) with a monolayer of gold after reaction, in vacuum, to as high a temperature as 735 K, did not restore the reactivity to any noticeable extent. The fact that the reactivity of a "spent" surface could partially be regenerated by an oxygen treatment is consistent with both poisoning mechanisms, as oxygen can react with carbon as well as with hydrogen. Thus this experiment does not discriminate between both possibilities.

The observed reactivity enhancement is also not an artifact of a coverage induced variation of the induction time in the reaction rate at the beginning of the reaction at 373 K, since the induction time does not correlate with the adsorbate metal coverage in either of the two systems, although it shows some variation from experiment to experiment.

In summary, the induction time and the self-poisoning are qualitatively the same for all cases, but quantitatively the induction times are longer and the self-poisoning rates lower for Au on Pt(100) than for Pt on Au(100). In both systems, however,

the induction times and self-poisoning rates are independent of the adsorbate metal coverage. The rates of benzene formation are, on the contrary, strongly dependent on the adsorbate metal coverages. The amount of carbon that is deposited by the reaction on a Pt(100) surface decreases to below the AES detection limit of about 3% when the gold coverage reaches the monolayer without changing the self-poisoning behavior.

4.2. The gold on Pt(100) system

There could be several possible causes for the observed reactivity enhancement of a Pt(100) single crystal surface by gold.
(a) Gold on top of the platinum could provide the active sites for the reaction. Gold has a lower work function than platinum and could donate electrons to the platinum. This would shift the charge density of the gold overlayer towards the platinum, and it could conceivably become active for the cyclohexene dehydrogenation. Work function measurements for evaporated platinum—gold alloy films [27] do show at certain alloy compositions a minimum in the work function that is below the values of both gold and platinum. This is consistent with a charge transfer from the surface (which is enriched with gold) to the bulk. Thermal desorption measurements of H_2 and CO on evaporated platinum—gold films [28] and of H_2 on dispersed platinum—gold catalysts [29], however, do not show new chemisorption states or shifts of the desorption peak temperatures when platinum is alloyed with gold. Only the population of the various chemisorption states is affected.

It could still be argued that gold on a Pt(100) single crystal surface represents a unique case that has no analog in alloys or gives only an undetectably small contribution there. Currently XPS—UPS and thermal desorption studies of the Au on Pt(100) system are under way in our laboratory to help to answer these questions.
(b) Another possibility is that platinum atoms located below the gold layer could be the active centers for the cyclohexene dehydrogenation. As we have found [21], gold assumes the Pt(100) substrate lattice constant up to two monolayers of gold and, therefore, fits in exact registry on top of the substrate lattice. Examination of the structure of this square fcc(100) surface shows relatively large "holes" between the atoms in the surface layer through which the second layer atoms might still be able to interact with molecules from the gas phase. For comparison, the diameter of such a "hole" is 1.1 Å (based on the metallic radius of platinum), while the Van der Waals diameter of a hydrogen atom is 0.56 Å and the C—H bond length 1.0 Å.

The presence of the gold overlayer would modify the nature of bonding of cyclohexene to such a platinum site either electronically or sterically (or both), which might result in an actual enhancement of the reactivity of the platinum sites in the subsurface layer. One way to test this hypothesis would be to use a Pt(111) surface as a substrate. The "holes" in this surface are only 0.37 Å in diameter, which could give rise to a different alteration of the reactivity as compared to what we observed on the surface with (100) orientation These experiments have not yet been carried out, however.

(c) A third possible explanation for the enhanced reactivity assumes that the active sites for the reaction are platinum atoms that have not been covered by gold, i.e. defect sites in the gold layer. The bonding at these sites would be modified by the presence of gold in a similar way as in the preceding case. As a consequence, the actual reactivity enhancement (expressed per surface platinum atom instead of per surface atom) would be larger than 6 by a factor equal to the inverse of the concentration of defect sites. A small concentration of defects in the gold layer would not have been detected in our AES and LEED characterization of these surfaces. It can be calculated, though, that the number of cyclohexene molecules that impinges on this small number of defect sites per unit time is too low to cause the observed reaction rates, even at a reaction probability of unity (actually about 2/3 of the total number of surface atoms has to be active). If, however, the surface residence time of a molecule of cyclohexene that impinges on a gold atom is long enough to allow diffusion to and subsequent reaction on a defect site, this objection will no longer hold.

When the turnover frequency of the benzene formation is integrated over the reaction time, extrapolating to infinite reaction time, the total number of turnovers per surface atom is obtained. In order for a reaction to be catalytic the total number of turnovers per surface atom N has to be "large", at least significantly greater than unity. For the benzene formation on Au on Pt(100), a maximum value of N of about 1 is found at the gold monolayer coverage (after correction of the ion gauge sensitivity for cyclohexene and benzene using data from ref. [30]). If one of the explanations (a) or (b) is correct, the reaction studied is not catalytic, under our reaction conditions. If explanation (c) applies, the total number of turnovers per surface atom has to be divided by the concentration of active sites (i.e. the concentration of defect sites), in which case the reaction may well be catalytic, depending on the actual concentration of defect sites (which, however, could not be determined in our experiments), and the minimum value for N that one still considers to be catalytic.

One more point has to be considered. As mentioned before, deposition of gold blocks the reaction path that leads to the formation of the surface carbon which amounts to about 1/2 monolayer on the pure Pt(100) surface. It may be that the cyclohexene molecules that would form these carbonaceous species on the gold covered platinum surface now also yield benzene which would give rise to an increase in the reactivity. However, 1/2 of a monolayer of carbon which contains 2 carbon atoms per surface atom [26] would only correspond to a benzene formation with a total number of turnovers per surface atom of $N = 1/6$, which is much too small to explain the observed 6-fold reactivity enhancement.

4.3. The platinum on Au(100) system

Platinum does not form smooth films on a Au(100) surface through the completion of successive monolayers, but grows as small three-dimensional crystallites [21].

This may be the cause of the larger scatter of the reactivity points in fig. 4 as compared to those of the Au on Pt(100) system, fig 3, since the detailed morphology of these microcrystallites may vary somewhat from deposition to deposition. Another consequence of the crystallite growth mechanism is that at least at coverages not exceeding one monolayer equivalent, the dispersion of the platinum is less than in the case of monolayer film growth. Nevertheless, at a coverage of one mle the reactivity of Pt on Au(100) is much larger than that of a Pt(100) single crystal surface. It may well be that the platinum edge atoms in those crystallites are more reactive than platinum atoms in a flat surface. Another possibility is that an electronic interaction between platinum and gold could alter the reactivity of the former. LEED characterization of these surfaces has given indications that the platinum may assume the Au(100) substrate lattice constant, which is 4% larger than that of the platinum [21]. If this is the case, it might influence the electronic structure of the platinum which could cause an altered bonding to hydrocarbons that could lead to the observed reactivity enhancement. For this system, as for Au on Pt(100) (see section 4.2) the total numbers of turnovers per surface atom is at most on the order of one and, consequently the cyclohexene dehydrogenation to benzene over platinum on Au(100) cannot be considered to be a catalytic reaction under our experimental conditions.

Acknowledgement

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