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Cyclohexane Dehydrogenation Catalyzed by Bimetallic Au–Pt(111) Single-Crystal Surfaces

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Cyclohexane dehydrogenation was investigated using two-phase, epitaxial Au on Pt(111) single crystal surfaces and single-phase Au–Pt(111) surface alloys as catalysts, with 20-mbar cyclohexane and 133-mbar H_2 at 573 K. Benzene production was found to be strongly enhanced by Au, reaching a maximum at a surface composition of 50 atom% Au and declining thereafter. The clean Pt(111) crystal face did not produce detectable amounts of cyclohexene, its formation by the single crystal being completely attributable to the crystal edges. The addition of gold to the Pt(111) surface also induced production of cyclohexene. Surfaces containing about 90 atom% Au were the most active. In both cases, the effects were similar for epitaxial and alloy surfaces, but the latter usually gave larger enhancements. The enhancement by Au of the cyclohexane dehydrogenation to benzene is interpreted as a reduction of the product poisoning of Pt sites by benzene. This, and the observation that only Au containing Pt(111) surfaces produced cyclohexene are both explained by ensemble size effects.

1. INTRODUCTION

Hydrogenation and dehydrogenation reactions play important roles in catalytic reforming of hydrocarbons over dual functional platinum on alumina catalysts. It has long been known that the metal function establishes the alkane/alkene equilibrium by catalyzing hydrogenation and dehydrogenation (*1*). The olefins are then isomerized and cracked on the acidic sites of the support, by carbenium ion mechanisms. However, Pt itself has also been found capable of catalyzing these reactions that had originally only been ascribed to the acidic support (*2*). Still, (de-)hydrogenation reactions on Pt are much faster than skeletal rearrangements and survive the longest when Pt is progressively poisoned by the deposition of coke.

With the advent of bimetallic reforming catalysts, such as Pt–Re (*3*), Pt–Ir (*4*), and Pt–Sn (*5*), it has become important to investigate the effects of the second metal on the (de-)hydrogenation properties of Pt. As these reactions are catalyzed by the metal function of the bifunctional reforming catalyst, it is preferable to conduct such studies under conditions where support effects are absent. In fundamental studies aimed at understanding the influence of the second metal it is advantageous to use combinations of metals with substantially different catalytic properties in order to separate the contributions from the two components. In a combination of two catalytically active metals, the role of mixed ensembles may greatly complicate the analysis of experimental data. However, their effect will be much smaller in a combination of an active and a much less active metal. Examples of systems which offer these advantages are combinations of group VIII–Ib metals.

In an investigation of the *n*-hexane conversion catalyzed by well-defined bimetallic Au–Pt(111) (*6*) and Au–Pt(100) (*7*) single-crystal surfaces we have found that the addition of Au to Pt gave rise to an enhancement of the dehydrogenation activity.

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However, accurate kinetic data could not be obtained as conversions very rapidly approached the maximum level permitted by the hexane/hexene equilibrium. As far as this could be judged in view of this restriction, this enhancement appeared to resemble those observed by Sinfelt *et al.* and Engels *et al.* for cyclohexane dehydrogenation, and Beelen *et al.* for cyclopropane hydrogenation over Ni–Cu alloys (*8*). Many other examples of similar effects are known.

In this paper, the results are presented of an investigation of the cyclohexane dehydrogenation catalyzed by well-defined bimetallic Au–Pt(111) single-crystal surfaces. With cyclohexane as a reactant, conversions are not limited by low values of the equilibrium constant at the reaction conditions used (20-mbar cyclohexane, 133-mbar H_2, 573 K). The temperature was the same as in our earlier *n*-hexane studies. This reaction was studied both with two-phase epitaxial Au on Pt(111) surfaces and with single-phase Au–Pt(111) surface alloys. While both types of surfaces have the same crystallographic structure, they have been found to display very different catalytic properties for skeletal reactions of *n*-hexane. This has been attributed to the difference in Pt ensemble sizes in these two types of surfaces (*6*).

2. EXPERIMENTAL

2.1. Apparatus

The experiments were carried out in an ultra-high vacuum (UHV) system equipped with an internal sample isolation cell to permit in-situ reaction studies at pressures up to 1 bar. Details of the apparatus have been described elsewhere (*9*). The sample isolation cell was connected to an external gas recirculation loop, forming a well-stirred batch reactor with a volume of 0.463 liter. Gases were recirculated through the reactor by a Teflon gear pump, samples were taken by a gas sampling valve and analyzed by a gas chromatograph equipped with a flame ionization detector.

Surface characterization was accomplished with four-grid electron optics used for low energy electron diffraction (LEED) and for the collection and analysis of Auger electrons emitted from the sample. The Auger electrons were excited by the electron beam from a separate gun, positioned at a near glancing angle of incidence with respect to the sample surface. Additionally the surfaces could be characterized by temperature programmed desorption (TPD). A quadrupole mass spectrometer was used to record the TPD spectra. The bimetallic surfaces were prepared by vapor deposition of Au onto the platinum single-crystal samples. The effusive type Au source and the evaporation geometry were the same as in earlier studies (*10*). Details of the sample mounting arrangement have been described elsewhere (*6*, *11*).

2.2. Materials

The platinum single crystal was prepared by spark erosion of a thin wafer from a high purity Pt single crystal rod, within 1° of the desired orientation as determined by Laue back-reflection X-ray diffraction. The wafer was polished mechanically on both sides and etched briefly in aqua regia before mounting in the vacuum chamber. The cyclohexane (Matheson) was found, by gas chromatographic analysis, to have a purity of 99.95 mole% with methylcyclopentane and *n*-hexane as impurities. It was degassed before use by repeated freeze-pump-thaw cycles. The high purity hydrogen, obtained from the Lawrence Berkeley Laboratory, was passed through a molecular sieve trap before use.

2.3. Procedures

The procedures for cleaning the Pt(111) single-crystal surfaces, preparing the epitaxial Au on Pt(111) layers and Au–Pt(111) surface alloys, as well as the procedures for characterizing these surfaces and performing the reaction studies have been described elsewhere (*6*, *10*).

Since a batch-type reactor was used, kinetic data of the catalytic reactions were obtained in the form of total accumulated product-versus-time curves. Initial reaction rates were obtained by graphical determination of the initial slopes of these curves. Unless otherwise noted, reaction rates and amounts of products have always been calculated as numbers of molecules produced per *total* number of surface atoms, Au + Pt. In this way singularities in the calculations were avoided for surfaces apparently not containing any Pt. Compared to platinum, the activity of Au is negligible for the reactions studied in the present work. The cyclohexane conversion was carried out with 20-mbar cyclohexane and 133-mbar H_2 at 573 K.

Before and after reaction, the surface compositions were checked using Auger electron spectroscopy. Before reaction, the surfaces were always free of contaminants. After 3 h of reaction, substantial amounts of carbon and, in some cases, traces of sulfur were detected. The trace amounts of sulfur (0–3% of a monolayer) are considered insignificant, and did not show any correlations with the kinetic data.

3. RESULTS

3.1. *Characterization of the Bimetallic Surfaces*

For the sake of clarity the most relevant results of our characterization of these surfaces (published elsewhere (*6*)) will be described briefly. Using Auger electron spectroscopy (AES), it was found that the deposited Au formed films on the Pt(111) single-crystal surface through a layer-by-layer (Frank–van der Merwe) growth mechanism. Further, it was shown with TPD of CO that at submonolayer coverages the Au adatoms formed two-dimensional islands leaving relatively large patches of the Pt(111) substrate uncovered. Contrary to these large Pt ensembles in the epitaxial surfaces, much smaller ensembles were found to predominate in the Au–Pt(111) surface alloys.

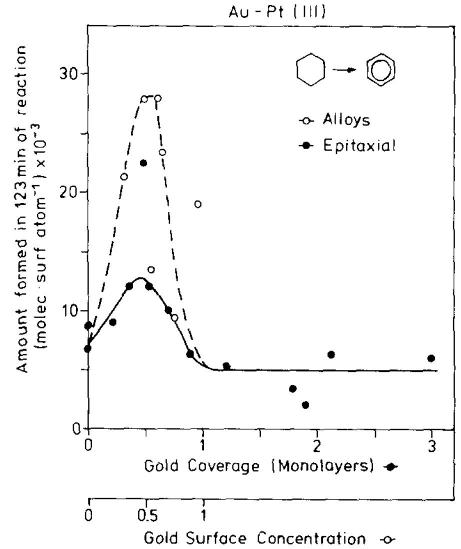

FIG. 1. Influence of Au surface content on the amount of BZ produced from CH in 123 min reaction time. A formation of 2.8 × 10^4 molecules BZ per surface atom corresponds to a CH conversion of 14.3 mole%.

3.2. *Cyclohexane Conversion*

Under the reaction conditions used, cyclohexane (CH) was converted into benzene (BZ), cyclohexene ($CH^=$), and very small amounts of *n*-hexane and smaller hydrocarbons. However, the latter two classes of reactions were several orders of magnitude slower than dehydrogenation and will not be discussed here. The influence of Au on the amount of BZ formed in 123 min reaction time is shown in Fig. 1. Note that two different abscissa are used in Figs. 1 and 2 for the data of alloy and epitaxial surfaces. The latter could also have been plotted against the gold surface concentration, but then all data at gold coverages larger than or equal to one monolayer would have been compressed into one vertical line at a gold concentration of 100%. This would be disadvantageous for the presentation of the results in some cases. The most striking feature of Fig. 1 is the enhancement of the BZ formation by gold, which reaches a maximum at a surface gold content of about 50%. The enhancement was observed both with the epitaxial and

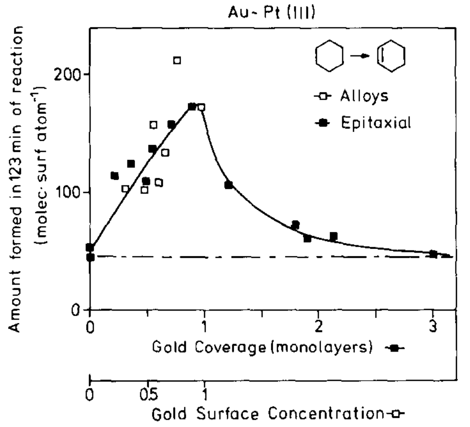

FIG. 2. Variation of the amount of $CH^=$ produced from CH in 123 min reaction time, with surface Au content.

the alloy surfaces, although it was generally larger with the surface alloys. Similar enhancements with maxima at Au surface concentrations of 50% were also found for the *initial* rates of BZ formation (not shown). At these maxima, the initial BZ formation rates per surface *Pt* atom exceeded those of the pure Pt(111) surface by factors of about 4.5 and 9 for epitaxial and alloy surfaces, respectively, after correcting for the contributions from the crystal edges which could not be covered by Au. These edges gave rise to the nonzero activities observed at high Au coverages, the catalytic activity of Au being negligible relative to that of Pt.

Figure 2 shows the influence of Au on the formation of $CH^=$ from CH, for the amounts formed in 123 min reaction time. Again, the contributions from the crystal edges to the total amounts of reaction product can readily be identified by the activity remaining at high Au coverages. Interestingly, it becomes evident from Fig. 2 that the pure Pt(111) crystal faces did not produce detectable amounts of $CH^=$. This product was apparently only formed by Pt(111) faces that had been modified by Au, either in the form of an epitaxial overlayer or as a surface alloy. In this case the maximum enhancement was found at a surface Au concentration of about 90 atom%, which differs significantly from the composition that gave maximum BZ production (Fig. 1).

The surface alloys also showed the same effects as in Fig. 2 for the *initial* rates of $CH^=$ formation; the epitaxial surfaces gave a smaller enhancement with a broader maximum.

3.3. *Formation of Strongly Bound Carbonaceous Species*

During hydrocarbon reactions, platinum surfaces always become covered by strongly bound, partially dehydrogenated carbonaceous species. In the apparatus used here, the amount of this "surface carbon" present on the catalyst after the CH reaction was determined from the C-272 eV, Pt-237 eV, and Au-246 eV Auger transitions. Quantification of the coverages was achieved by using the calibration from Ref. (*12*) (for C on Pt) while further assuming that this calibration would be the same for C on Au. This approximation appears reasonable since the Pt and Au Auger spectra are very similar, in the region near 240 eV even practically identical. Thus, it was observed that the amount of surface carbon present after the CH reaction decreased with increasing Au concentration, from a value of 1.0 monolayer for the pure Pt(111) surface to a constant value of 0.7 monolayer for surfaces containing 1.0 or more monolayers of Au. Within the scatter of the data of ±0.15 C-monolayers, the decrease appeared to be linear with Au surface concentration. The surface alloys seemed to remain slightly cleaner than the corresponding epitaxial surfaces; however, this difference may not be significant in view of the fairly large scatter of the data.

4. DISCUSSION

4.1. *Cyclohexane Dehydrogenation to Benzene*

The observation that alloying a catalytically active group VIII metal with a much less active Ib metal leads to enhanced dehydrogenation of cyclohexane is not unique for the Au–Pt(111) system, but has also been reported for, e.g., Cu–Ni alloys (*8*) and, to a lesser extent, for Cu–Ru bimetallic clusters (*13*). These changes of the catalytic activities may be caused by two different effects (*14*). On the one hand, the intrinsic activity of the sites that catalyze the reaction may be altered. On the other hand, and this is always an important consideration with hydrocarbon reactions, alloying may inhibit the side reactions, such as deep dehydrogenation leading to coke formation, that cause poisoning of the catalyst surface. In this case the number of active sites available to catalyze the reaction may increase without a change of their intrinsic activity. With respect to the CH dehydrogenation to BZ, Sinfelt *et al.* suggested that the reaction on pure Ni was inhibited by strong adsorption of the product on the catalyst surface, blocking sites (*8a*). Herz *et al.* investigated the CH dehydrogenation catalyzed by a number of different Pt single-crystal surfaces (*11*). Most of their experiments were carried out under the same reaction conditions as used in the present work. They found that the BZ formation per unit surface area of the catalyst increased with increasing degree of coordinative unsaturation of the surface, in the order smooth Pt(111) < stepped Pt(557) < kinked Pt(10,8,7) < highly kinked Pt(25,10,7) single-crystal surfaces. Herz *et al.* also investigated the deactivation of these catalysts during reaction and distinguished two different poisoning mechanisms, viz., deactivation due to product inhibition and poisoning of the catalyst surface by the accumulation of strongly bound carbonaceous species. By comparing the inhibiting effect of the addition of aromatic molecules to the reaction mixture with the deactivation during a normal reaction run they found product poisoning to be clearly structure sensitive, increasing in magnitude in the order Pt(25,10,7) < Pt(10,8,7) < Pt(557) < Pt(111). This indicates a correlation between the activity of these surfaces and their sensitivity to product poisoning. No clear structure dependence was found for the deactivation by strongly bound carbonaceous species. Further, the contribution of the latter poisoning mechanism to the total catalyst deactivation was found to be smaller than that of product poisoning by strong BZ adsorption, at least in the first 2 h of reaction. At this point it should be noted that in the experiments by Herz *et al.*, as well as in ours, batch-type reactors were used in which the reaction products accumulate with time. Thus, in these systems more pronounced deactivation by strong product adsorption may occur than in open flow systems in which the products are continuously removed.

Somorjai *et al.* observed that steps and kinks were more active than terrace atoms in $CH^{=}$ dehydrogenation to BZ catalyzed by Pt single-crystal surfaces at low pressures. During this reaction, the terraces and flat Pt(111) surfaces were always covered by a complete monolayer of partially dehydrogenated hydrocarbon species (*15*). Similarly, Lehwald *et al.* also identified steps as active sites for CH dehydrogenation by Ni, and found that BZ only adsorbed on the terraces (*16*). Herz *et al.* further found a positive reaction order in H_2 for the CH reaction, which would seem quite surprising for a dehydrogenation reaction. This could indicate that the rate-determining step involves a relatively deeply dehydrogenated species, which could be a reaction intermediate that has to be (partially) rehydrogenated before further reaction or desorption can take place. Alternatively, this species might just block the surface, thereby reducing the number of available active sites. Higher hydrogen pressures would then cause a faster CH conversion by keeping the surface cleaner. All these data are consistent with a model according to which the CH dehydrogenation is limited by rehydrogenation and desorption of dissociatively adsorbed BZ, C_6H_x with x decreasing in the order Pt(25,10,7) > Pt(10,8,7) > Pt(5,5,7) > Pt(111). This is further in agreement with the observation by Herz *et al.* that at 573 K CH dehydrogenation remained positive order in hydrogen over the entire pressure range studied (133–800 mbar) with Pt(111), but that the reaction order in H_2 dropped to zero at 400 mbar with the kinked Pt(10,8,7) surface (*11*).

There are several more direct pieces of evidence that support this idea of dissociative adsorption of BZ. Davis found that the hydrogen content of BZ, adsorbed on Pt(111), Pt(100), and Pt(10,8,7) single-crystal surfaces at 300 K, decreased when the layer was heated in vacuum. After heating to 600 K the average composition of the layer was reduced to C_6H (*17*). Under our reaction conditions, the presence of 133-mbar H_2 probably reduced the extent of the dissociation but may not have been able to completely prevent it. Lehwald *et al.* found that BZ adsorbed on Ni(111) even decomposed below 400 K (*16*). On Ni films, the self-poisoning of the BZ hydrogenation has also been ascribed to dissociative adsorption of BZ (*18*) and the effects of temperature and hydrogen pressure have been discussed in Ref. (*18b*). However, this dissociative adsorption of BZ need not be irreversible. Basset *et al.* found that BZ, adsorbed on Pt, could be rehydrogenated with hydrogen to CH after the reaction cell had been evacuated at 623 K (*19*). From the data cited above (*17*), it follows that the adsorbed BZ had been substantially dehydrogenated. Further, dissociative BZ adsorption has been postulated to explain kinetic isotope effects of H_2–C_6D_6 and D_2–C_6H_6 exchange reactions on Ni and Pt (*20*). Using ^{14}C-labeled molecules, Davis *et al.* demonstrated that partially dehydrogenated BZ on a Pt(111) single-crystal surface can be rehydrogenated with gas-phase hydrogen or also by hydrogen transfer from other hydrocarbon molecules (*17*). However, the more extensively dehydrogenated the adsorbed layer was, the smaller the fraction was that could be rehydrogenated (*12b*).

In view of all the data and arguments presented above, it appears most likely that alloying Pt with Au influences the CH dehydrogenation by restricting the number of Pt atoms available for interaction with adsorbed BZ. This prevents deep dehydrogenation of the adlayer, reducing the self-poisoning of the reaction and thereby enhancing the BZ production. Evidence for this hypothesis can be found in results of Puddu *et al.* who investigated catalytic hydrogenation over Pt–Au alloy powders (*21*). They found complete suppression of BZ hydrogenation on the most diluted alloys, which, however, still catalyzed $CH^=$ hydrogenation. From this they concluded that the hydrogenation of BZ to CH requires larger ensembles than the $CH^=$ hydrogenation to CH. According to the principle of microscopic reversibility, this ensemble requirement should also hold for the reverse reaction, i.e., dehydrogenation of CH and $CH^=$ to BZ. Consequently, the following picture emerges. When Pt(111) is alloyed with small amounts of gold, deep dehydrogenation of BZ no longer takes place and the product poisoning is reduced or even eliminated. The resulting activity increase is larger than the reduction of the active Pt surface area. At an intermediate gold surface concentration, the activity reaches a maximum and declines thereafter as the ensembles are becoming too small to catalyze CH dehydrogenation down to BZ.

Based on the interpretation of previously published results for the *n*-hexane skeletal reactions catalyzed by the same Au–Pt(111) surfaces as used in the present work, the above-mentioned ensemble size effects on the CH dehydrogenation would not be expected for the epitaxial Au on Pt(111) surfaces (*6*). However, the data in Fig. 1 also show an enhancement for the epitaxial system, which would appear to contradict the proposed explanations of the effects of Au. This is an important problem that needs to be clarified before a complete understanding of these systems can be reached. However, the following considerations may help to clarify this apparent discrepancy. It should be noted that the conclusion that epitaxial Au layers only inhibit hydrocarbon reactions in proportion to the Au coverage, was based on data for the *skeletal* reactions of *n*-hexane (*6*). As has been briefly mentioned in Ref. (*6*), the dehydrogenation of *n*-hexane was actually enhanced by Au. In resemblance to the present CH data, it was found that alloys gave larger enhancements than epitaxial Au layers. However, those observations were only of a qualitative nature as the initially high olefin formation rates for the bimetallic surfaces decreased rapidly, in some cases vanishing in only a few minutes reaction time. Thus, it appears that the influence of epitaxial Au islands on catalyzed hydrocarbon reactions may vary according to the nature of the reactant hydrocarbon. In this respect, it is very interesting to note that a quite similar phenomenon has been observed for pure Pt single-crystal surfaces, viz., with respect to the effects of steps and kinks on hydrocarbon reactions. Specifically, the CH dehydrogenation to BZ has been found to be enhanced by steps and kinks on the Pt surface, while skeletal reactions of *n*-hexane did not show this type of structure sensitivity (*11, 17*). Davis *et al.* demonstrated for a Pt(557) surface that this is due to the fact that, unlike CH, *n*-hexane very rapidly poisons the Pt steps (*26*). Thus, these data suggest that for these types of reactions a great similarity exists between Pt surfaces with Pt steps (and kinks), and Pt surfaces with Au steps (and possibly kinks) formed by the Au-island edges. It may then be speculated that the adsorption of BZ near a Au-island edge would be perturbed and therefore weakened relative to an unmodified Pt(111) surface. Consequently, the rate of CH dehydrogenation to BZ would initially increase with Au coverage as the total Au-island edge area increases, and at some point begin to decrease as the Au islands coalesce. With *n*-hexane as a reactant, the Au-island edges might become poisoned in a relatively short time, leading to the absence of lasting effects of Au other than site blockage. Clearly, more research is needed to substantiate this speculation. Further, it needs to be clarified why a specificity for the chemical identity of these structural defects is lacking, and whether this behavior is only a coincidence for the systems studied here, or possibly a phenomenon with a more general validity.

4.2. Cyclohexane Dehydrogenation to Cyclohexene

The data presented in Section 3 do not only show enhanced BZ formation, but an increase of $\mathrm{CH}^{=}$ formation as well. Actually $\mathrm{CH}^{=}$ is a new product since its production by a clean Pt(111) crystal only originated from the crystal edges. The explanation of the $\mathrm{CH}^{=}$ formation on alloy surfaces is an extension of the argument used above to explain the BZ enhancement. As the Pt ensembles decrease in size with increasing gold surface concentration, the cyclohexene-like intermediate that is formed during the CH dehydrogenation is no longer quantitatively converted to BZ but it desorbs as $\mathrm{CH}^{=}$. Consequently, the maximum of its formation is reached at higher gold concentrations than that of BZ. The enhancement by epitaxial Au islands can similarly be ascribed to small Pt ensembles in this case consisting of uncovered Pt atoms in defects that are always present in small concentrations in the epitaxial Au layer. These defects only become covered after deposition of several monolayers which is why one gold monolayer seems to have a high activity. The poisoning of the defect sites at high gold coverages seems to be slower than that of the small ensembles in the surface alloys, since although the epitaxial surfaces initially form $\mathrm{CH}^{=}$ at lower rates than the alloys, the amounts formed in 123 min reaction time are essentially the same for both types of surfaces (Fig. 2).

In the preceding part of the discussion it has been attempted to explain the observed effects purely by geometric effects. Alternatively, a ligand effect may be invoked to explain the observed enhancements. Thus, the intrinsic bonding abilities of Pt and Au could in principle be altered by an electronic interaction between the two elements, consisting of charge transfer or some other effects. In general, such interactions are expected to be largest in bimetallic systems with large positive heats of formation (*22*). Thus, larger ligand effects are expected for an exothermic alloy such as, e.g., Pt–Cu than for endothermic alloys such as Ni–Cu and Pt–Au. However, XPS data indicate the absence of electronic effects in the Pt–Cu system (*23*). An investigation of the frequency shift of the infrared absorption band of CO, caused by alloying Pt with Cu, using ^{12}CO and ^{13}CO showed that the observed frequency shift can completely be accounted for by geometric, i.e., dilution effects (*24*). Further, no ligand effect was found in a study of TPD of CO on the same Au–Pt(111) surfaces as used in this investigation (*6*). In our opinion, these data all leave little room for speculations on the significance of any kind of "electronic" or "ligand" effects in the present system, although in the literature these are frequently used to explain analogous enhancements of catalytic activity by alloying.

4.3. Formation of Irreversibly Adsorbed Carbonaceous Residues

The work by Herz *et al.* has shown that under the conditions used here, product poisoning by BZ is the predominant deactivation mechanism. However, they also observed poisoning by the accumulation of strongly bound carbonaceous residues (*11*). In the present work, the influence of Au on the coverage by carbonaceous species that are bound so strongly to the surface that they do not desorb in UHV, even after heating to 573 K, has been studied with AES. The most significant result is that, as with the *n*-hexane conversion (*6, 7*), even completely Au covered surfaces did not remain clean. This is surprising since Au is known for its relative inertness for chemisorption and catalysis. An investigation by Chesters *et al.* using flat (111) and stepped 6(111) × (100) Au single crystal surfaces with hydrocarbon pressures up to 10^{-6} mbar and temperatures up to 823 K failed to find any adsorption of hydrocarbons such as CH$^{=}$ and BZ (*25*). However, naphthalene was adsorbed dissociatively yielding strongly bound hydrocarbon fragments. This indicates that Au is not incapable of forming these overlayers, but that the activation energy of this process is high for relatively light hydrocarbons. In the CH reaction described in this work, the hydrocarbon pressure was 7 orders of magnitude higher than in the just mentioned chemisorption study, and this enormous increase of the hydrocarbon exposure might well have been sufficient to give the less than one monolayer carbonaceous species on Au despite the low reaction probability for this process.

CONCLUSIONS

(i) Under the reaction conditions used, Au was found to enhance the cyclohexane dehydrogenation to benzene catalyzed by Pt(111) single-crystal surfaces, with surfaces containing about 50 atom% Au being most active.

(ii) This enhancement is attributed to a reduction, by Au, of reaction self-poisoning caused by dissociatively adsorbed benzene.

(iii) Under the reaction conditions used, cyclohexene is not desorbed during cyclohexane conversion by pure Pt(111) crystal faces. However, bimetallic Au–Pt(111) surfaces do produce substantial amounts of cyclohexene, with a maximum for surfaces containing about 90 atom% Au.

(iv) Cyclohexene production by the bimetallic surfaces occurs on sites where subsequent dehydrogenation to benzene is inhibited by ensemble size restrictions.

(v) The observed effects of Au are similar both for the epitaxial and the alloy Au–Pt(111) surfaces, which is in contrast to the large differences between these two types of surfaces with respect to skeletal reactions of *n*-hexane. This variability of the effect of epitaxial Au islands appears to follow that of the "step effects" of pure Pt surfaces for these reactions.

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