JOURNAL OF CATALYSIS **103**, 208–212 (1987)

Surface Structure Sensitivity of Alloy Catalysis: Catalytic Conversion of *n*-Hexane over Au–Pt(111) and Au–Pt(100) Alloy Crystal Surfaces

Alloys have become important catalysts for many chemical processes due to their superior properties over single component catalysts. These include increased reaction selectivity and greater resistance to deactivation. The reasons for their superior performance are not well understood, however. Catalytic studies, using single component metal single crystal catalysts, coupled with the use of surface science techniques, have proven useful in understanding the nature of the working catalyst (*1–4*). Extension of these investigations to alloy single crystal at high pressures should be useful for elucidating the role of alloying in altering catalytic behavior (*5*). In this note we report the surface structure sensitivity of the catalytic properties of platinum–gold alloys in the conversion reaction of *n*-hexane and present evidence for a mixed Au–Pt site on the (111) surface for the isomerization reaction.

Experiments were carried out in an ultrahigh vacuum system equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED) optics, a quadrupole mass spectrometer, and a sample isolation cell which was connected to the reactor loop and gas chromatograph equipped with a flame ionization detector. Details of the system have been reported elsewhere (*6*). Single crystal alloy surfaces were prepared by the deposition of several monolayers of gold from a Knudsen cell-type evaporation souce (*7*) onto the surface of a platinum single crystal of either (111) or (100) orientation. The gold-covered crystal was then annealed briefly at 1070 K to allow the diffusion of gold into the platinum substrate, forming a surface alloy. Characterization of the alloy surface was carried out using AES, CO thermal desorption, and LEED, as described previously (*8*). The sample was then enclosed in the isolation cell and the reaction gasses (20 Torr *n*-hexane, 200 Torr H_2) were introduced into the reactor loop. A reaction temperature of 566 K was used. Samples of the reaction gasses were taken at 20-min intervals and analyzed using gas chromatography. After 2 h of reaction, the reaction loop was evacuated and the isolation cell opened to UHV. The surface of the alloy was then analyzed.

The catalytic conversion of *n*-hexane was studied over the (100) surface of gold–platinum alloys. In Fig. 1a, the initial rates (initial rates *per surface atom*, i.e., gold and platinum) of isomerization (formation of 2- and 3-methylpentane), C-5 cyclization (formation of methylcyclopentane), aromatization (formation of benzene), and hydrogenolysis (formation of molecules containing 5 carbons or less) are shown as a function of surface alloy composition. The rate of C-5 cyclization decreased with a positive deviation from the linear, while isomerization and hydrogenolysis dropped off linearly with increasing surface atom fraction of gold. The rate of aromatization decreased rapidly with increasing surface atom fraction of gold, going nearly to 0 at a surface atom fraction of 0.5 gold.

The catalytic conversion of *n*-hexane over the (111) surface of platinum–gold alloys has been studied in our laboratory and reported previously (*8*). The results of that work are shown in Fig. 1b. The rate (*per surface atom*) of isomerization doubled as the surface atom fraction of gold was increased from 0 to 0.25. The rate then remained fairly constant between 0.25 and 0.75 and then rapidly dropped off to 0 when

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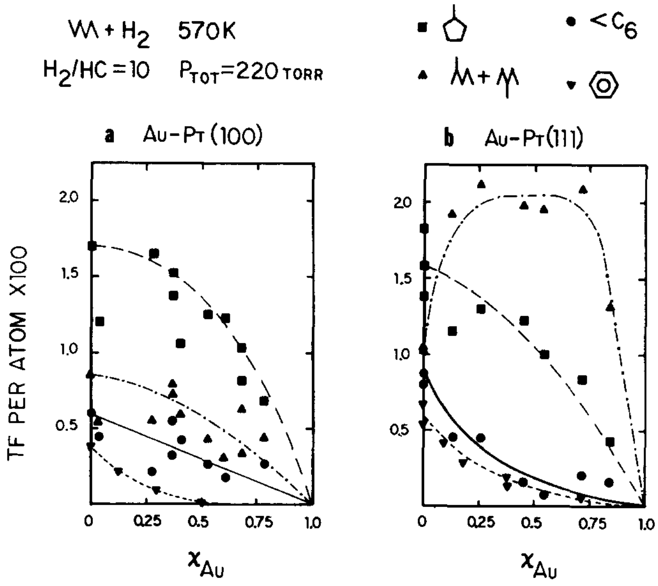

FIG. 1. A plot of the initial turnover frequencies per surface atom (*platinum and gold*) versus the surface atom fraction of gold.

the surface was completely covered with gold. The rate of hydrogenolysis and aromatization decreased rapidly with increasing surface atom fraction of gold, going nearly to 0 at a surface atom fraction of 0.5 gold. The rate of cyclization fell off nearly linearly with increasing surface atom fraction of gold.

These trends are more clearly seen in Fig. 2, where the initial turnover frequency *per surface platinum atom* is shown as a function of surface atom fraction of gold. For the Au–Pt(100) system (Fig. 2a) the rate of cyclization *per surface platinum atom* increased with increasing surface atom fraction of gold, while the hydrogen-

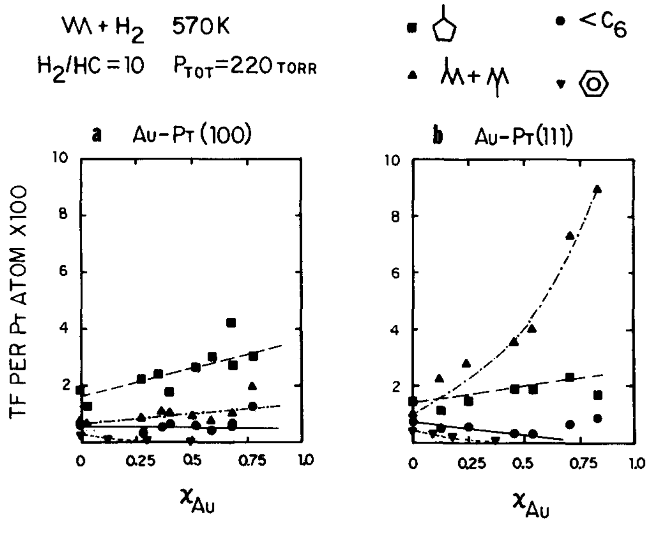

FIG. 2. A plot of the initial turnover frequencies per surface *platinum* atom versus the surface atom fraction of gold.

olysis and isomerization rates remained relatively constant, and the rate of aromatization decreased rapidly. Over the entire composition range, the probability of internal bond scission in the hydrogenolysis reaction remained constant at about 0.83. The ratio of 2-methylpentane to 3-methlypentane decreased from 1.8 for the platinum surface to ~1 for a high surface atom fraction of gold.

For the Au–Pt(111) surfaces (Fig. 2b) the isomerization rate *per platinum atom* increased greatly with increasing surface atom fraction gold and the cyclization rate increased only slightly. The rates of aromatization and hydrogenolysis dropped off rapidly with increasing surface atom fraction of gold.

The total activity after 2 h of reaction for both the Au–Pt(100) and Au–Pt(111) surfaces is shown as a function of surface composition in Fig. 3. The activity of the Au–Pt(100) alloy decreased linearly with increasing surface atom fraction gold. The Au–Pt(111) alloy showed an enhancement in the total activity as the surface atom fraction of gold was increased from 0 to 0.4, and then fell off with a further increase in the surface atom fraction of gold.

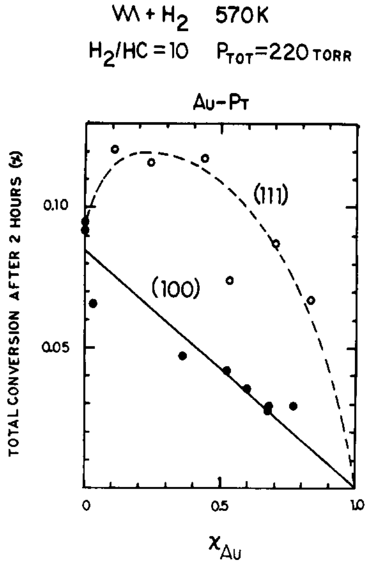

FIG. 3. The total conversion after two hours reaction for the (111) and (100) alloy surfaces as a function of surface atom fraction of gold.

Alloying of the Pt(111) and Pt(100) surfaces with gold drastically effected the activity and the selectivity of both the surfaces, however in different ways. Gold alloying increased the total activity of the Pt(111) surface up to a surface atom fraction of 0.4 gold and then the activity decreased. A decrease in the activity of the Pt(100) surface proportional to the surface atom fraction of gold was observed. The large difference in the behavior of the two orientations of the alloy surfaces, however, was seen in the selectivity of the reaction.

The results of the Au–Pt(111) surface have been interpreted in terms of the ensemble effect (*9*). Using these arguments, it appears that hydrogenolysis and aromatization require large ensembles of platinum atoms. The dilution of the platinum surface with gold reduces the number of these large ensembles, inhibiting these reactions. The blockage of these reaction pathways provides more surface species for the reactions which require only small ensembles of platinum atoms, i.e., cyclization and isomerization, resulting in a higher rate per platinum atom with increasing surface atom fraction gold. Since the major reaction pathway for the isomerization reaction on the Pt(111) surface is through a five-member ring (*10*), it is interesting that the isomerization rate increased upon increasing the surface atom fraction of gold from 0 to 0.25 while the cyclization rate decreased. This data indicates that the isomerization occurs not only via a cyclic intermediate but also by some other mechanism. It is also clear that the aromatization reaction does not occur on the metal through a ring enlargement of a five member ring.

The ensemble effect was again manifest in the behavior of the aromatization reaction on the Au–Pt(100) surfaces. The corresponding inhibition of the hydrogenolysis

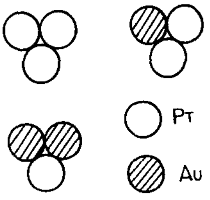

FIG. 4. Proposed active isomerization sites on the Au–Pt(111) alloy surface.

reaction was not observed, however, indicating a less severe ensemble size constraint for the hydrogenolysis reaction on the more open, fourfold (100) alloy surface. The reactions which required smaller ensembles again showed an enhanced rate per platinum atom, but there was only a very slight enhancement of the isomerization rate, in contrast to the (111) alloy surface. This would indicate that the second mechanism for isomerization which was observed for the (111) alloy surfaces was not available on the (100) alloy surfaces and that the opening of the five-member ring was suppressed, as indicated by the change in the ratio of 2-methylpentane to 3-methylpentane.

These contrasting results can only be explained by the creation of a new catalytic site for the isomerization reaction. Because the second mechanism was observed on the (111) surface and not the (100) surface, the new site must be a threefold site, since ontop and twofold sites were available on both surfaces, or else be due to the different electronic structures of the two surfaces. Also, the isomerization rate on the (111) alloy surface decreased rapidly at surface atom fractions of gold greater than 0.75, indicating that at least one platinum atom must be present at the three fold site, as illustrated in Fig. 4. The nature of the intermediate, however, cannot be determined at this time.

Another difference in the behavior of the two alloy surface orientations was manifest in the total activity of the surfaces. The results indicate that the Au–Pt(100) alloy surfaces are poisoned more rapidly by carbonaceous deposits than the Au–Pt(111) surfaces. Since the gold at the (100) alloy surface was unable to participate in the reaction, no increase in the overall activity of the catalyst was observed. The gold at the (111) alloy surface, however, provided a more active site for isomerization which resulted in an enhanced activity of the catalyst up to high surface atom fractions of gold.

While our explanations are tentative pending further investigations, our results clearly indicate the *structure sensitivity of alloy catalysis for hydrocarbon* conversion. Not only are the surface structure sensitivities of hydrocarbon conversion reactions that are observed for the single component metal surfaces show up on alloy catalysts but there are opportunities to form new mixed alloy sites that may introduce different reactivity behavior. Thus the effects of alloying a catalytically active metal with a catalytically inactive metal are complex and should be carefully explored using various surface structures of the active metal including stepped and kinked surfaces. Our results may also explain the lack of reproducibility of reaction selectivities when high surface area alloy catalysts that were prepared in different ways are compared (*11*).

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under Contract DE-AC03-75SF00098.

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Received May 3, 1985

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