Lawrence Berkeley National Laboratory

Recent Work

Title

SURFACE STRUCTURE SENSITIVITY OF ALLOY CATALYSIS: CATALYTIC CONVERSION OF n-HEXANE OVER Au-Pt(111) AND Au-Pt(100) ALLOY CRYSTAL SURFACES

Permalink

<https://escholarship.org/uc/item/3456g16q>

Authors

Yeates, R.
Somorjai, G.A.

Publication Date

1985-04-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAY 16 1985

LIBRARY AND
DOCUMENTS SECTION

Submitted to the Journal of Catalysis

SURFACE STRUCTURE SENSITIVITY OF ALLOY CATALYSIS:
CATALYTIC CONVERSION OF n-HEXANE OVER Au-Pt(111)
and Au-Pt(100) ALLOY CRYSTAL SURFACES

R. Yeates and G.A. Somorjai

April 1985

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks*

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-19454

SURFACE STRUCTURE SENSITIVITY OF ALLOY CATALYSIS: CATALYTIC
CONVERSION OF n-HEXANE OVER Au-Pt(111) AND Au-Pt(100)
ALLOY CRYSTAL SURFACES

R. Yeates and G.A. Somorjai

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, California 94720, USA

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 improved performance are not well understood, however. Catalytic studies, using single component metal single crystals, 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 crystals at high pressures should be useful for elucidating the role of alloying to alter 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 3-fold site that further enhances the rate of the isomerization reaction.

Experiments were carried out in an ultra-high 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 deposition of several monolayers of gold from a Knudsen cell-type evaporation source (7) onto the surface of a platinum single crystal of either (100) or (111) 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 reactant gases (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 gases were taken at 20 minute intervals and analyzed using gas chromatography. After 2 hours 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 carbon atoms 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, reaching nearly zero at a 0.5 surface atom fraction of 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 - 0.75 and then rapidly dropped off to 0 when the surface was completely covered with gold. The rates 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 mole 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 hydrogenolysis 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-methylpentane 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 hours 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 of 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.

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 mole 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 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 reaction was not observed, however, indicating a less severe ensemble size constraint for the hydrogenolysis reaction on the more open, four-fold (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 large increase observed over the (111) alloy surface. This would indicate that the new 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 2-methylpentane to 3-methylpentane ratio.

These contrasting results can only be explained by the creation of a new catalytic site for the isomerization reaction. Because the new mechanism was observed on the (111) surface and not the (100) surface, the new site must be a three-fold site, since on-top and two-fold sites were available on both surfaces. Also, the isomerization rate on the (111) alloy surfaces 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. This new site must, therefore, be a three-fold site which contains at least one

platinum atom, 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 poison more rapidly 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 structure sensitivities of hydrocarbon conversion reactions that are observed for 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 an 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).

REFERENCES

1. S.M. Davis, F. Zaera and G.A. Somorjai, J. Catal. 53(1983).
2. F. Zaera and G.A. Somorjai, J. Am. Chem. Soc., in press.
3. M. Asscher and G.A. Somorjai, Surface Sci. 143(1984)L389.
4. G.A. Somorjai and S.M. Davis, Platinum Met. Rev., 17(1983)54.
5. V. Poncet, Catal. Rev.-Sci. Eng. 11(1975)41.
6. D.W. Blakely, E.I. Kozak, B.A. Sexton and G.A. Somorjai, J. Vacuum Sci. Technol. 13(1976)1091.
7. J.W.A. Sachtler, M.A. Van Hove, J.P. Biberian and G.A. Somorjai, Surface Sci. 110(1981)19.
8. R.C. Yeates and G.A. Somorjai, Surface Sci. 134(1983)729.
9. J.W.A. Sachtler and G.A. Somorjai, J. Catalysis 81(1983)77.
10. F.G. Gault, in "Advances in Catalysis", Vol. 30, D.D. Eley, H. Pines and P.B. Weisz, eds., Academic Press, New York, 1981 p. 1.
11. G.K. Boreskov, Kinet. Catal. (USSR), 10(1969)7.

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

FIGURE CAPTIONS

- Fig. 1 A plot of the initial turnover frequencies per surface atom (platinum and gold) versus the surface atom fraction of gold.
- Fig. 2 A plot of the initial turnover frequencies per surface platinum atom versus the surface atom fraction fo 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.
- Fig. 4 Proposed active isomerization sites on the Au-Pt(111) alloy surface.

$\text{W} + \text{H}_2$ 570K
 $\text{H}_2/\text{HC} = 10$ $P_{\text{TOT}} = 220 \text{ TORR}$

XBL 854-2028

Fig. 1

XBL 854-2029

Fig. 2

$\text{W} + \text{H}_2$ 570K
 $\text{H}_2/\text{HC} = 10$ $P_{\text{TOT}} = 220 \text{ TORR}$

XBL 854-2031

Fig. 3

ACTIVE SITES FOR HEXANE ISOMERIZATION

XBL 854-2030

Fig. 4

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720