HOKKAIDO UNIVERSITY

| | |
|---|---|
| Title | CHEMISORPTION AND CATALYTIC ACTIVITY OF A SET OF PLATINUM CATALYSTS |
| Author(s) | AIKA, K.; BAN, L. L.; OKURA, I. et al. |
| Citation | JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 24(1), 54-64 |
| Issue Date | 1976-09 |
| Doc URL | https://hdl.handle.net/2115/25007 |
| Type | departmental bulletin paper |
| File Information | 24(1)_P54-64.pdf |

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

*J. Res. Inst. Catalysis Hokkaido Univ., Vol. 24. No. 1, pp. 54 to 64 (1976)*

# CHEMISORPTION AND CATALYTIC ACTIVITY OF A SET OF PLATINUM CATALYSTS

By

K. AIKA*), L. L. BAN**), I. OKURA*), S. NAMBA*)
and John TURKEVICH*)

(Received February 23, 1976)

**Abstract**

Procedures have been developed for the preparation of monodisperse platinum sols by the reduction of chloroplatinate ion by citrate ion, for hydrothermal preparation of ultramicroscopic alumina plates and for the preparation from these of platinum on alumina catalysts. These catalysts and platinum on silica catalysts prepared both by impregnation and ion exchange and obtained from Professor BURWELL were characterized by high resolution electron microscopy, electron diffraction, chemisorption and determination of active centers for ethylene hydrogenation by poison titration with sulphur compounds. Good relationship for the number of surface atoms was obtained between electron microscopy and hydrogen chemisorption. However the number of active centers for hydrogenation was found to be a fraction of the number of surface atoms determined by hydrogen chemisorption. Platinum sols of varying sedimentation constants were found to have varying catalytic activity for hydrogen peroxide decomposition and this activity paralleled their light absorbance in solution before coagulations set in.

## Introduction

Platinum has been the most important precious metal catalyst with a history starting with the manufacture of sulfuric acid, ammonia oxidation, hydrogenation both on industrial and laboratory scale, reforming to produce high octane gasoline and, recently, as a catalyst for the complete combustion of automobile exhaust gases. It is usually used supported on high surface area alumina, silica or charcoal. The method of preparation of a highly active catalyst is an art. Usually the support is soaked with a soluble platinum salt and then heat treated in the presence or absence of a reducing gas to produce small particles of metallic platinum. The particle size and

*) Frick Chemical Laboratories, Chemistry Department, Princeton University, Princeton, New Jersey 08540, USA.
**) Cities Service Company, Petrochemicals Research, Cranbury, New Jersey 08512.

the distribution of the particles on the support are of primary importance in determining the value of the preparation in catalytic processes. It is well established that particles whose diameter is greater than 100 Å are not very active. Consequently, it is desirable to optimize the distribution in the range of diameters less than 100 Å. Furthermore, with a metal as precious as platinum, the finer the particle size the more platinum atoms will be on the surface where they are active.

The impregnation procedure for preparing supported catalysts, though almost universally used, involves complex topochemical processes whose individual steps cannot be separated and consequently cannot be controlled. It is difficult to determine whether the reduction of the salt to the metal is complete, whether the particles formed are all available for catalytic action or are buried in the deep pores of the support granule and whether the particles are clumped. The preparation of alloy catalysts by impregnation of a support with a salt of at least two metals raises the question whether an alloy is actually formed or whether the two metals coexist as individual particles.

To avoid these difficulties a program was initiated at Princeton to prepare the platinum in solution as a monodisperse sol, the alumina support as thin long plates about 280 Å × 1000 Å and adsorb the platinum onto the alumina in suspension. The catalyst so prepared may be dried directly or itself adsorbed onto a carrier such as corundum granules or massive honeycomb matrix. The advantage of colloidal plate-like alumina as a support is that on evaporation it produces a "haystack" containing large pores of great mechanical strength, permitting ready ingress of reactants and egress of products, thus optimizing the availability of all platinum particles to the reactants. Furthermore, electron microscopic examination of platinum particles on thin alumina plates permits examination of platinum and support over holes in the usual carbon supporting membrane thus avoiding artifacts due to the carbon membrane. This work with platinum on alumina is an extension of a series of Princeton researches on the synthesis of and properties of colloidal metal particles, alumina, and silica, and catalytic activity of these.[1)]

In addition to these preparations, studies were carried out on a series of platinum on silica catalysts made available to us by Professor Robert BURWELL of Northwestern University.

The particle size determination was made by ultracentrifugation, high resolution electron microscopy, and by chemisorption of hydrogen at 25°C.[2)] The number of active centers was obtained by progressive poisoning tech-

nique at 0°C for the reaction of ethylene hydrogenation.[3] Catalytic activity was determined for the homogeneous hydrogen peroxide decomposition and correlated with sedimentation constants and light absorption. The consistency of particle size determination by various techniques[4] was examined. Furthermore, the relations between the number of surface atoms and number of catalytic centers obtained by poisoning was investigated.

## Experimental

The platinum sols were prepared in the following way using doubly distilled water in all operations. A two-liter round bottom flask was cleaned with aqua regia, rigorously washed and charged with 960 ml. of water. It was brought to boiling by an electric heating mantle and 60 ml. of chloroplatinic acid solution (60 mg. Pt Engelhard Industries 40% Pt) were added. The solution was again brought to the boiling point and 120 ml. of 1 wt % sodium citrate (certified grade Fischer Scientific Co.) were added. The reaction mixture was again brought to boiling. A series of color changes was observed —the bright light yellow color disappearing and the solution gradually acquiring brownish black color. After four hours' boiling, the solution was cooled in ice-water bath and stored in a refrigerator. This sol could be de-ionized by stirring with Amberlite MB–1 ion exchange resin.

Alumina plates were prepared by hydrothermal treatment in a pressure reactor with a glass liner of 10 grams of colloidal alumina (duPont Baymal) in 1 liter 0.05 M acetic acid. This sol was also de-ionized with Amberlite MB–1 resin.

The platinum-on-alumina plates catalyst was prepared by contacting the platinum sol with the de-ionized alumina sol and centrifugation.

The platinum on silica catalysts were obtained from Professor R. BURWELL of Northwestern University. They were prepared either by exchange with $Pt(NH_3)_4$ ion or by impregnation of the silica with $H_2PtCl_6$.

A high resolution electron microscope (Philips EM–300, Philips Electronics, Inc., Mount Vernon, N.Y.) using 100 kV and capable of resolution of about 1.2 Å was used to characterize the particles and the supports.

Chemical analysis of platinum was carried out on all catalyst samples by procedure of AYRES and MEYER.[5]

## Results and Discussion

The four hour platinum sol labelled as standard was found by electron microscopy to have particles with an average diameter of 34 Å with deviation

**Plate 1.** Overall Transmission Electron Micrograph of Standard 32 Å Platinum of Plate-like Alumina.

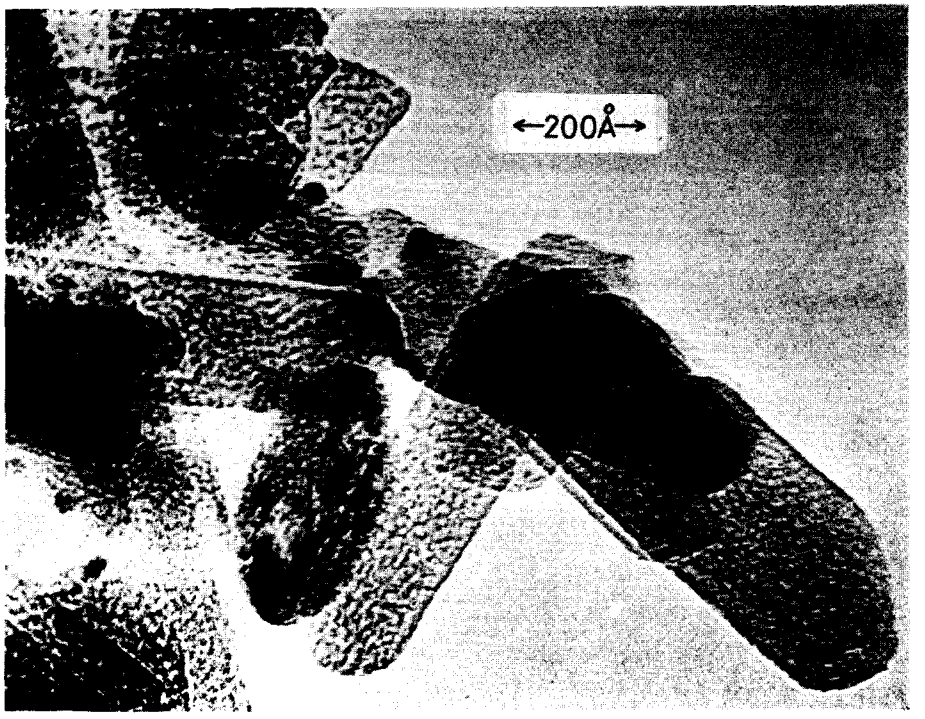


**Plate 2.** Detail Transmission Electron Micrograph of Standard 32 Å Platinum on Plate-like Alumina.

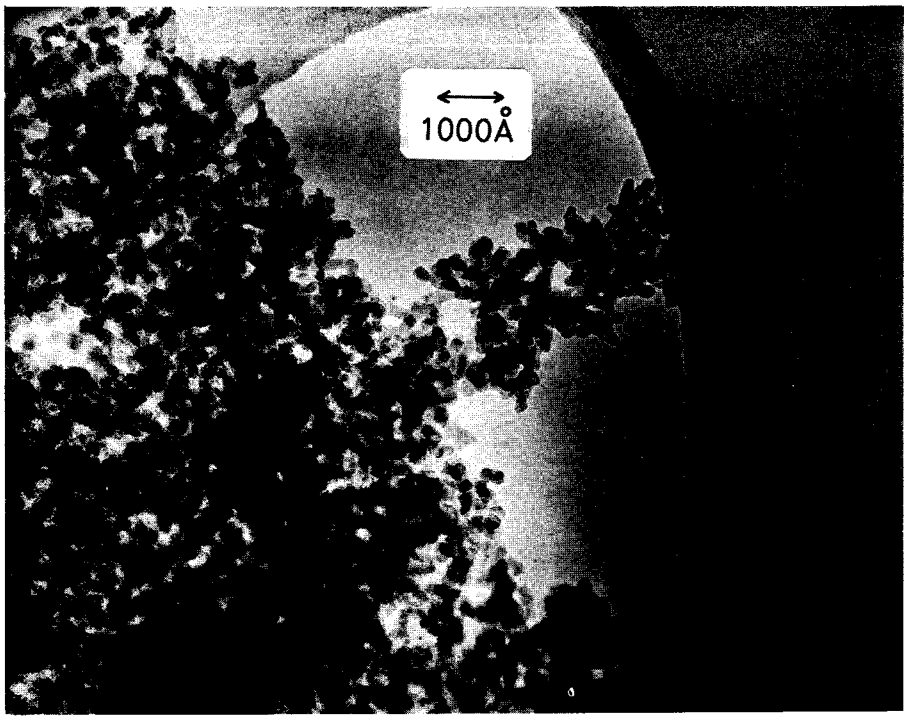


**Plate 3.** Overall Transmission Electron Micrograph of No. 67 Platinum on Silica Catalysts. Particles of Platinum have 19 Å Diameter.

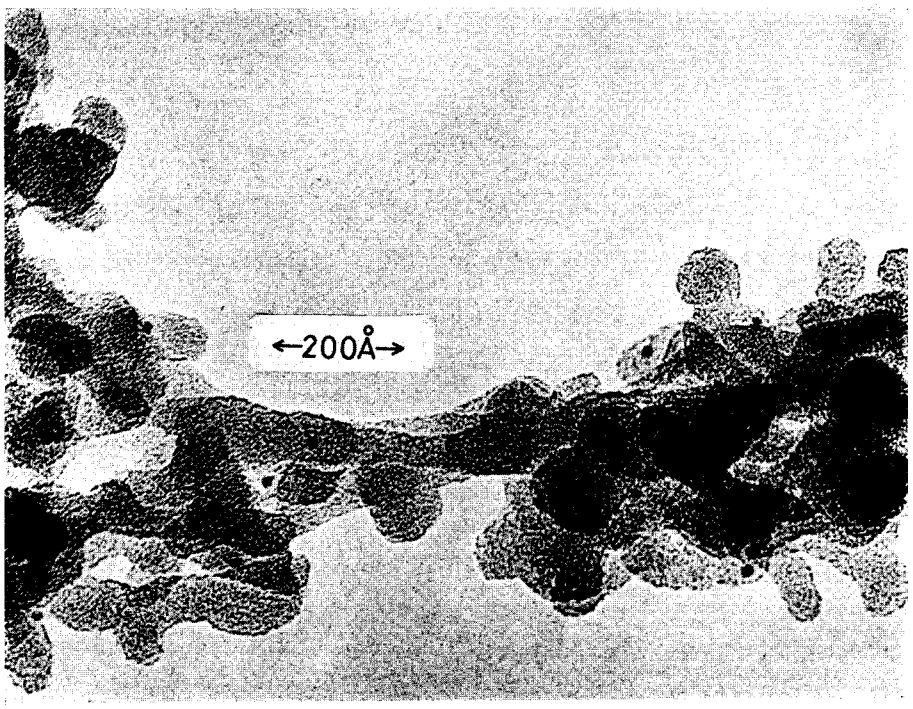


**Plate 4.** Detail of Transmission Electron Micrograph of No. 67 Platinum on Silica.

from the mean of 25%. Under ultrahigh resolution when mounted on carbon films their shape was not spherical. Individual spots of about 3 Å could be discerned which might be considered as clusters of platinum atoms were it not for the fact that the carbon substrate on which the platinum sol was mounted produced artifacts which made atomic identification speculative. Electron diffraction rings were obtained with d spacing of 2.25 Å (strongest and markedly spotted), 1.93 Å (weak with some spots), 1.38 Å (weakest), and 1.15 Å (broad and diffuse). Metallic platinum shows diffraction rings at 2.27 Å (111 plane), 1.96 Å (200) and 1.15Å (222). The 1.38 Å diffraction may be due to the 200 plane and the diffuse 1.15 Å coincides with the one obtained from the carbon supporting membrane. Thus, the electron diffraction results confirm that the standard platinum sol mounted on carbon film consists of metallic platinum particles.

Ultracentrifugation gave a sedimentation constant of 120 to 160 svedbergs. Using the density of metallic platinum as 21.45 this corresponds to particles of 34 to 37 Å in good agreement with electron microscopic determination. The sol was stable in the refrigerator for several months.

The standard platinum sol had a brownish black color with the following absorbances: 0.74 at 400 nm, 0.63 at 450 nm, 0.56 at 500 nm, 0.50 at 550 nm, 0.44 at 600 nm, 0.38 at 650 nm, and 0.32 at 700 nm. Using simplified absorption and scattering theory we calculate absorbances that are an order of magnitude smaller than the observed values although they show the same general wavelength dependence. Whether this discrepancy is due to the inadequacy of the theory or due to unusual electronic properties of small particles cannot be determined at the present time. It should be pointed out that for gold sols of much larger size (200–1200 Å diameter), excellent agreement was obtained between theory and experimental results.

Electron microscopic examination of 0.5 wt % standard platinum sol particles on platelike alumina showed particles of 34 Å average size with standard deviation of 11% well distributed on the alumina without clustering (plates 1 and 2). Furthermore, assuming that one surface atom adsorbs one hydrogen atom, chemisorption gave a dispersion value of 36% which corresponds to a diameter of 33 Å.

In an attempt to prepare platinum particles of varying size, the standard sol preparation was stopped at various times by rapidly quenching the hot solution in an ice-water bath. There were slight variations in experimental results from run to run but representative data is presented in Figure 1. The sedimentation constants increase in a regular way suggesting production

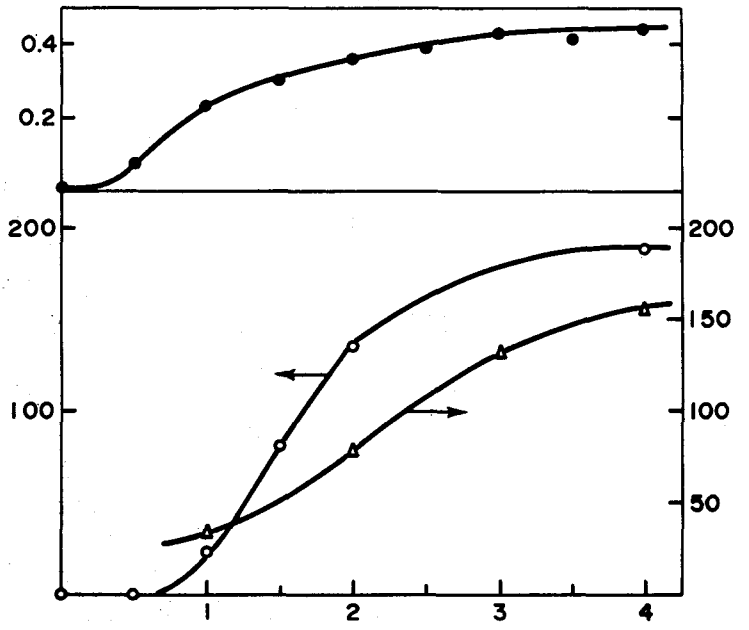


**Figure 1.** Typical Variation of Hydrogen Peroxide Decomposition Catalytic Activity, Optical Absorbance at 600 nm, and Sedimentation Constant with Time of Preparation of the Platinum Sol
Abscissa: Preparation Time in hours
Ordinate: left bottom: $H_2O_2$ Decomposition Activity ($min^{-1}m\ell(mg\ cat)^{-1}$)
left top: Absorbance at 600 nm
right: Sedimentation Constant in Svedbergs.

of platinum particles of increasing size. The optical absorbance dependence on wavelength was similar to that of the standard platinum sol but had a low value at one hour and increased steadily with the preparation time. Chemical analysis of the sol at various times of preparation indicated that after ion exchange and sol coagulation by 10% NaCl, more than 80% of the platinum was in the colloidal particles. Thus, the increase in the sedimentation values is not due to growth of particles but is the result of coagulation of small platinum-organic colloidal particles and subsequent formation of metallic platinum sol. Electron microscopic examination of the samples mounted on carbon film showed a variety of diffuse particles of about 30 Å diameter which were coagulated in various shapes. To account for the observed sedimentation rate, their density must be about 3 and not 21.45 characteristic of metallic platinum.

Mounting the one hour sol on alumina produced metallic particles of about 29 Å average diameter with standard deviation of 10% as determined

microscopically and 32 Å by hydrogen chemisorption; for the two hour preparation the value is 36 Å. These results indicate that the standard sol preparation consists of the formation of a diffuse organo-metallic precursor colloid in the first hour and its coagulation and decomposition into metal during the subsequent three hours. These precursors are very prone to coagulation both on being mounted on carbon film for electron microscopy and on adsorption onto alumina plates. In solution these precursor colloids were sufficiently stable to permit carrying out hydrogen peroxide decomposition studies. The rate of decomposition for various times of preparation is given in Figure 1. The reaction temperature was 24.5°C, the hydrogen peroxide concentration was 0.6 to 0.75 wt %, the catalyst concentration was 210 nano grams/ml and the pH of the solution was 6.2. It is seen that the sol has no catalytic activity after 0.5 hour and very slight activity at 1.0 hour of preparation. Then, however, the catalytic activity rises rapidly with preparation time. This rise is paralleled by increasing absorbance at 600 nm. Thus, the catalytic activity in these solutions is proportional to some electronic factor of the platinum.

The platinum silica samples obtained from Professor BURWELL showed excellent agreement for the dispersion values obtained by ourselves and his group (indicated in parenthesis). The agreement between the particle diameter obtained on the basis of chemisorption and electron microscopy was also good (plate 3, 4). Thus, No. 66 sample, prepared by impregnation with chloroplatinic acid, gave 36% (40%) with a diameter of 33 Å while the microscope value was 37 Å. Sample No. 67, prepared by ion exchange, had 62% (63.5%) dispersion giving 19 Å particles and the microscope measurement was 19 Å. Sample No. 70, ion exchanged and fired, gave 24% (27%) dispersion with particle diameter 49 Å compared to 47 Å by microscopy. The sample No. 88, obtained by impregnation and firing, gave 5% (7%) dispersion which would indicate the presence of 240 Å diameter particles. Electron microscopy revealed only small particles of about 30 Å. This discrepancy may be due to the imprisonment of platinum particles by coalescence of pore openings making the platinum unavailable for either chemisorption or catalytic activity.

The number of catalytically active centers was determined by titrating with carbon disulfide as a poisoning reagent, using the hydrogenation of ethylene as an indicator. The number of carbon disulfide molecules just necessary to poison the catalytic activity was taken as the number of active centers. This is given for a number of catalysts in Figure 2 as a function of the number of surface atoms as determined by hydrogen chemisorption.

It is seen that the number of active sites as determined by poisoning with carbon disulfide is but a fraction of those determined by chemisorption of hydrogen. This is not due to channeling in the flow reactor used in the poisoning studies since the titre of active centers does not depend on flow rate. Furthermore, the chemisorption of carbon disulfide corresponds to

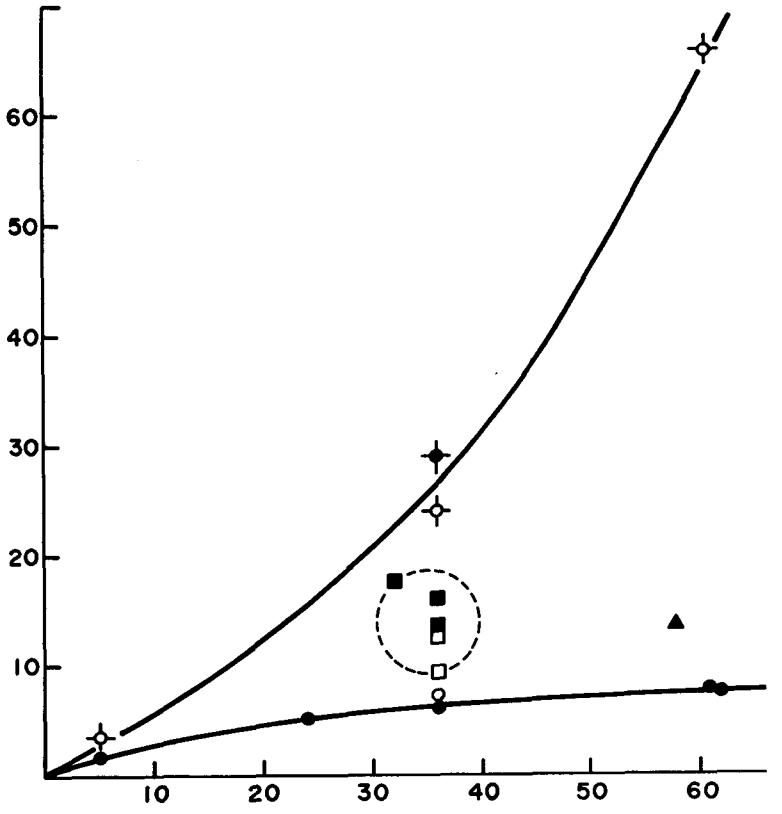


**Figure 2.** Relation between Hydrogen Chemisorption and Poisoning and Chemisorption by Sulphur Compounds.

Abscissa: Percent Platinum Acting as Hydrogen Chemisorbed Centers
Ordinate: Percent Platinum Atoms Acting as Poison or Chemisorbed Centers for Sulphur Compounds

Poisoning titration data for platinum on alumina indicated by filled squares and triangle for $CS_2$, chemisorption data for $CS_2$ by empty squares. Platinum on alumina Baymol preparations enclosed by dotted circle.

Poisoning titration data for platinum on silica indicated for $CS_2$ by filled circle, for $H_2S$ crossed empty circle, for $(CH_3)_2S$ crossed filled circle. Chemisorption by $CS_2$ is indicated by empty circle.

this titre. We found for No. 66 (platinum on silica) 6.1% active sites and 7.5% dispersion by carbon disulfide chemisorption; for one hour platinum on alumina we found 16% active centers by poisoning and 9.8% dispersion by carbon disulfide chemisorption. The four hour platinum on alumina had 13.7% active centers by poisoning and 12.6% dispersion by carbon disulfide chemisorption. Thus, the values for poisoning by carbon disulfide agree quite well with the values obtained by chemisorption of the same molecule. Furthermore, after carbon disulfide chemisorption the hydrogen chemisorption became negligible. Thus, in the case of platinum on silica No. 66, the 61% hydrogen chemisorption became 4% and for one hour platinum on Baymal alumina plates it dropped from 36% to less than 1%. Thus, chemisorption of carbon disulfide has a marked effect on hydrogen chemisorption. The behavior of carbon oxysulfide is similar to that of carbon disulfide. The effect of both of these poisons, immobilizing up to eight surface atoms, may be peculiar to these two substances. It may be a property of the poison and not of the platinum surface since the titre obtained using hydrogen sulfide as a poison gives a better correspondence between the active centers and the hydrogen chemisorption. The following measurements that illustrate this must be treated with caution since the acidic hydrogen sulfide may be adsorbed on whatever traces of alkali might remain on the silica and alumina. For example, No. 66 platinum on silica gave 36% dispersion by hydrogen chemisorption and 24% active centers by hydrogen sulfide titration. Sample No. 87 of platinum on silica gave 61% dispersion by hydrogen chemisorption and 66% active centers by hydrogen sulfide titration. Sample No. 88 gave 5% dispersion by hydrogen chemisorption and 3.6% by hydrogen sulfide poisoning. It was also found that dimethyl sulfide gave 29% active center by poisoning compared to 36% by chemisorption of hydrogen.

The behavior of hydrogen sulfide and dimethyl sulfide was not studied as extensively as that of carbon disulfide and will be subject to further investigation to see whether systematic errors may arise in adsorption measurements and poisoning titration due to adsorption on support or weak adsorption on metallic particles.

Thus, the question remains open whether the number of active sites on a surface is a property of the surface and the particle size, independent of the nature of a wide range of reactions or whether it is influenced to a dominant degree by the nature of molecules foreign to the reaction such as carbon disulfide.

**Acknowledgements**

We wish to thank Professor Robert BURWELL of Northwestern University for the standard platinum on silica sample. We also wish to express our appreciation to Dr. Robert S. MINER, Jr., for technical assistance in this investigation, to Miss Bardara BAUMAN for ultracentrifuge work, and to Dr. D. E. WHITE, Dr. T. H. VANDERSPURT and Dr. L. Gonzales TEJUCA for work which served as the basis of this investigation and which will be reported elsewhere. This investigation was carried out with the support of the United States Energy Research and Development Agency and its predecessor, the United States Atomic Energy Commission.

**References**

1) J. TURKEVICH, J. Chem. Phys., **13**, 235 (1945).
J. TURKEVICH and J. HILLIER, Anal. Chem., **21**, 475 (1949).
J. TURKEVICH, H. H. HUBBELL and J. HILLIER, Disc. Faraday Soc., **8**, 348 (1950).
J. TURKEVICH and H. H. HUBBELL, J. Amer. Chem. Soc., **73**, 1 (1951).
J. TURKEVICH, P. C. STEVENSON and J. HILLIER, Disc. Faraday Soc., **11**, 55 (1951).
J. TURKEVICH, G. GARTON and P. C. STEVENSON, J. Colloid Sci. Suppl., **1**, 26 (1954).
J. TURKEVICH, American Scientist, **47**, 97 (1959).
J. TURKEVICH and Y. S. CHIANG, J. Colloid Sci., **18**, 772 (1963).
J. TURKEVICH and B. V. ENUSTUN, J. Amer. Chem. Soc., **85**, 3317 (1963).
J. TURKEVICH and G. KIM, Science, **169**, 873 (1970).
J. TURKEVICH, S. DEMIRCI and D. J. SKVIR, Croatica Chimica Acta, **45**, 85 (1973).
2) J. E. BENSON and M. BOUDART, J. Catalysis, **4**, 704 (1965).
3) J. TURKEVICH, F. NOZAKI and D. STAMIRES, *Proceedings of the Third International Congress on Catalysis*, Amsterdam, 1964, Vol. 1, p. 586.
J. TURKEVICH and G. KIM, Science, **169**, 873 (1970).
4) G. R. WILSON and W. K. HALL, J. Catalysis, **24**, 306 (1972).
P. RATNASAMY, A. J. LEONARD, L. RODRIGUE and J. J. FRIPIAT, J. Catalysis, **29**, 374 (1973).
5) G. H. AYRES and A. S. MEYER, Anal. Chem., **23**, 299 (1951).