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Catalytic Activity of an Evaporated Platinum Film Progressively Poisoned with Arsine*

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The activity of an evaporated platinum film catalyst for the hydrogenolysis of cyclopropane was a linear function of the amount of arsine adsorbed on the surface. The adsorption of poison was measuerd directly by suspending the catalyst from a microbalance. The mechanism of the poisoning as determined from catalytic activity, from kinetics of adsorption, from activation energies with progressive poisoning, and from the BET area appears to be the sintering of the platinum by arsine, probably to form platinum arsenide. A simplified model is proposed to interpret the data.

The manner in which poisons affect the activity of catalysts can be used to obtain information about the nature of the catalyst surface and the role of the catalyst during the process of catalysis. A number of such studies have appeared in the literature.

Maxted and co-workers (*1–7*) have performed extensive poisoning studies. Their work was aimed primarily at determining the homogeneity of catalyst surfaces with respect to activity, the toxicity of various poisons, and methods for reactivating poisoned catalysts.

Among other studies reported in the literature, Morris and Selwood (*8*) found a linear correlation between the magnetic susceptibility and the catalytic activity of nickel-activated copper which decreased with increasing poison content. They concluded that the poison affects approximately 10% of the nickel atoms, presumably those on the surface of the microcrystals.

Herrington and Rideal (*9*) made a theoretical analysis to determine the general shape of a poisoning curve for a homogeneous catalyst. They showed that the assumption of a heterogeneous surface is not necessary to explain selective poisoning (poisoning the surface for one reaction, but not for another) or a nonlinear change in catalyst activity with poison content. A linear change would occur only when one surface site is required for the rate-determining step.

Campbell and Thomson (*10*) found that mercury poisoned a nickel film for the hydrogenolysis of cyclopropane, but not for the hydrogenation of propylene. They reported a nonlinear change in catalyst activity with poison content.

Brill and Tauster (*11*) found that the ammonia synthesis reaction appeared to be proportional to the second power of the fraction of the unpoisoned catalyst surface. They interpreted that result to mean that two surface sites are required for the rate-determining step, which is consistent with the widely accepted activated adsorption of nitrogen.

Recently some investigators (*12, 13*) estimated the concentration of active centers in various catalysts by using poisoning techniques. Balandin *et al.* (*14*) poisoned an evaporated platinum film to indicate that the hydrogen–deuterium exchange in cyclohexane occurs by means of both a "doublet and a sextet mechanism."

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In virtually all of the studies cited, the toxicity of the poisons was attributed to their ability to displace preferentially reactants from active centers. Furthermore, in the work cited, only Campbell and Thomson (*10*) directly measured the amount of poison adsorbed on the catalysis.

In the present work, the activity of a platinum film catalyst for the hydrogenolysis of cyclopropane was measured as a function of the amount of poison adsorbed by the catalyst. The adsorption of poison was measured directly. In addition to determining the effect of the poison on catalytic activity, the kinetics of the poisoning process and the physical state of the poisoned catalyst were also investigated. The objective was to learn what physical and chemical changes in the catalyst cause deactivation.

The hydrogenolysis of cyclopropane,

$$\mathrm{(CH_2)_3} + H_2 \longrightarrow CH_3{-}CH_2{-}CH_3\ ,$$

was selected as the test reaction because kinetic data can be obtained at room temperature and there are normally no side products. The kinetics of this reaction have been studied extensively (*15–24*) and the reported orders of the reaction vary from 0 to 1.0 with respect to cyclopropane and from —1.0 to 0 with respect to hydrogen. The orders depend primarily on the preparation of the catalyst and the temperature of the reaction. The reported values of the activation energy vary from 8.0 to 12.2 kcal/gmole-°K.

Experimental Apparatus and Procedure

The experimental reactor and associated apparatus used are shown in Fig. 1. The main parts of the apparatus are a recirculating, batch-type reactor, a microbalance and a chromatograph. The reactor volume is about 2.6 liters and the reaction mixture is recirculated at approximately 4 liters/min past a catalyst which is suspended from the microbalance by a quartz fiber. To prevent reactants and products from accumulating in the microbalance chamber, a purge stream of 9 ml/min swept through the 3-mm orifice separating the reactor and microbalance chamber. A purge of the same volumetric flow rate left the reactor and was routed through the chromatographic sampling valve and subsequently to the atmosphere. The initial conversion in the reactor was about 0.1% per pass.

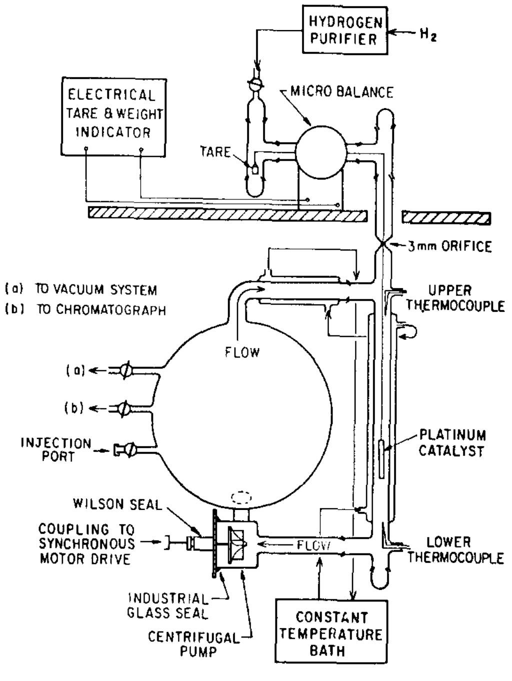

Fig. 1. Schematic diagram of purged reactor system.

The reactor was maintained at constant temperature by enclosing it in styrofoam insulation and circulating water from a constant-temperature bath through the jackets around the catalyst chamber. The temperature of the reactants was measured with two copper-constantan thermocouples positioned above and below the catalyst.

The hydrogen used was purified by diffusion through a Milton Roy palladium thimble. Cyclopropane (99.5% minimum purity) obtained from the Matheson Company was purified further by a single-stage distillation in which the first and last thirds were discarded. Arsine, diluted to 0.5% by volume in hydrogen (99.999% pure), also supplied by the Matheson Company, was utilized as a poison.

A pure platinum catalyst was used in this work to eliminate uncertainties in interpreting poison adsorption on a dual-site catalyst. Platinum foil and wire do

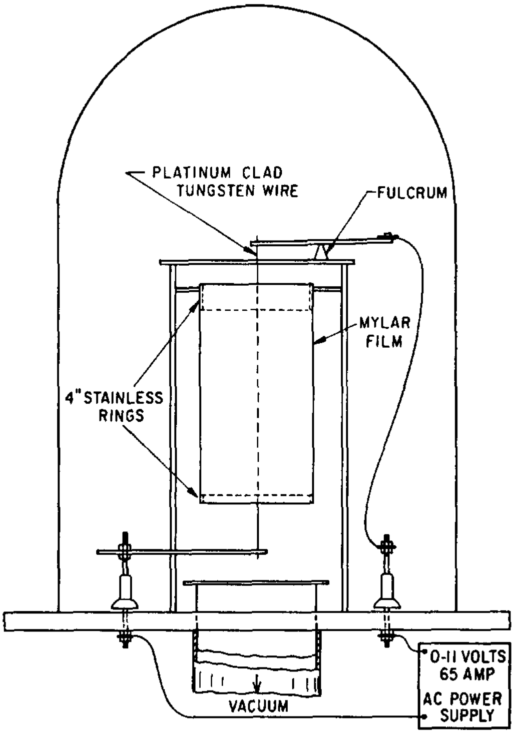

Fig. 2. Apparatus for evaporating platinum on Mylar films.

not have enough specific surface area to meet the 1-g weight limit of the microbalance, and the surface area of pelletized platinum black was not thermally stable. Therefore, platinum film evaporated on Mylar film was used because it met the requirements of stability and large area per unit weight. The apparatus used for the vapor deposition is shown in Fig. 2.

After measuring the BET surface area, the catalyst was activated by alternately exposing it to air and hydrogen at room temperature. The reactor was first evacuated to 10^{-6} torr and then filled to 10 torr with air. After the weight stabilized (5 min), the system was again evacuated and filled to 150 torr with hydrogen. The system was again evacuated and filled to atmospheric pressure with hydrogen and was continually purged with hydrogen thereafter. The effectiveness of each activation attempt was checked by making a kinetic run with hydrogen and cyclopropane and the procedure was repeated until maximum activity was attained. Two repetitions were generally required.

After the activation step, a series of 16 runs were made to determine the activity and the stability of the catalyst for the hydrogenolysis reaction. During the first 10 kinetic runs the catalytic activity increased 10%. Then the catalyst weight remained relatively stable and the kinetic activity of the film remained constant to within 2%. The sequential poisoning of the film was then started. Further details on the apparatus and procedure are given in Ref. (*32*).

Results

The platinum catalyst was progressively poisoned by injecting small doses of the

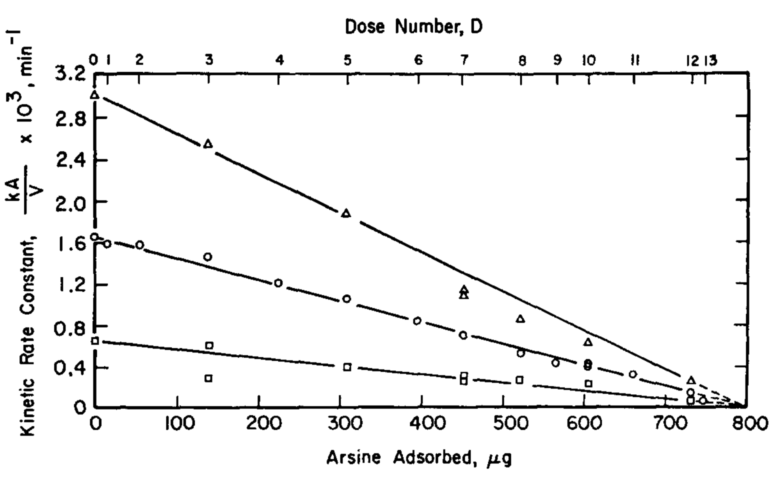

Fig. 3. Kinetic rate constants as a function of the quantity of arsine adsorbed on film B.

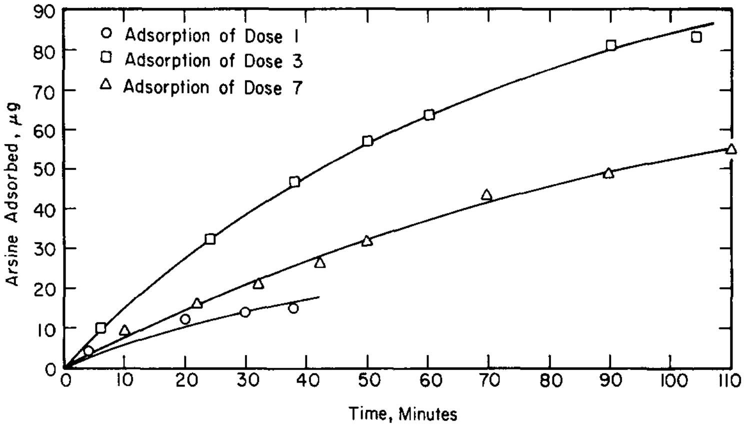

FIG. 4. First-order curves fit to adsorption data.

arsine–hydrogen mixture through a serum cap into the reactor with a Hamilton gas syringe. Catalytic activity was measured at 25°C following each addition of arsine. Following 6 of the 13 doses of arsine injected, additional kinetic runs were made at 56 and 2.5°C, which permitted the activation energy to be followed as a function of the amount of arsine adsorbed on the catalyst.

The apparent first-order kinetic rate constant, k', for the hydrogenolysis of cyclopropane was used as a measure of catalytic activity, and it decreased approximately linearly with poison content, as shown in Fig. 3. This linear behavior was not expected since virtually all investigators have reported a nonlinear change in activity with poison content. The significance of the linear decrease in activity observed in this work will be discussed later. The reported rate constant, k', is related to the intrinsic rate constant, k, by the ratio of V/A, i.e., $k' = kA/V$. The initial value of V/A is 0.72 cm.*

Before the meaning of this curve is discussed it is essential to know how accurately the adsorption of arsine was measured and how uniformly it was adsorbed. The weight was monitored directly throughout the entire series of runs by means of a microbalance. The weight of arsine was determined by the weight change recorded over a period of several hours exposure to a metered dose of arsine. Note that although arsine is continually removed from the system by the hydrogen purge stream, 50–75% of the arsine added was adsorbed by the catalyst. The stability of the microbalance over a several-hour period is of the order of a microgram, whereas the arsine adsorbed per dose was about 50–60 μg. These direct measurements were added consecutively to determine the abscissa of Fig. 3, and totaled 747 μg for the 13 doses of arsine. The overall difference between the initial and final weights of the catalyst after the 2-month run represented in Fig. 3 is 783 μg. The agreement is excellent and one might infer that the arsine adsorption is known to about 5%.

After completion of the poisoning, the film was analyzed for uniformity of arsine adsorption, using a 3-m Baird Spectrograph. A 2-cm^2 section was cut out of the film every 4 cm along the length for a total of seven samples. Each sample contained approximately 10 μg of arsenic and concentration differences could not be detected. The spectrometric line densities could only be read within a factor of two and the estimated total amount of arsine agreed with the microbalance results to within about a factor of two.

The kinetics of the adsorption were obtained from the weight–time history during adsorption. Since the adsorption approximated a first-order process, an equation was derived (*32*) for obtaining a first-order adsorption rate constant, $k'_a = k_aA/V$, by fitting the micrograms of arsine

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* V is taken as the volume of the reactor vessel below the orifice of 2598 cm^3 and A is taken as the initial BET area of 0.36 m^2.

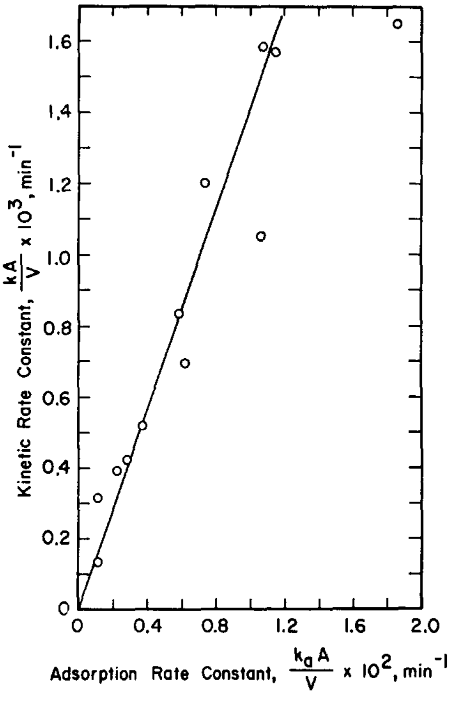


FIG. 5. Correlation between kinetic and adsorption rate constants, both at 25°C.

adsorbed, n_A^*, as a function of the micrograms of arsine in the reactor, n_A.

$$n_A^* = \frac{n_A k'_a}{k'_a + \kappa}\{1 - \exp[-(k'_a + \kappa)t]\}. \quad (1)$$

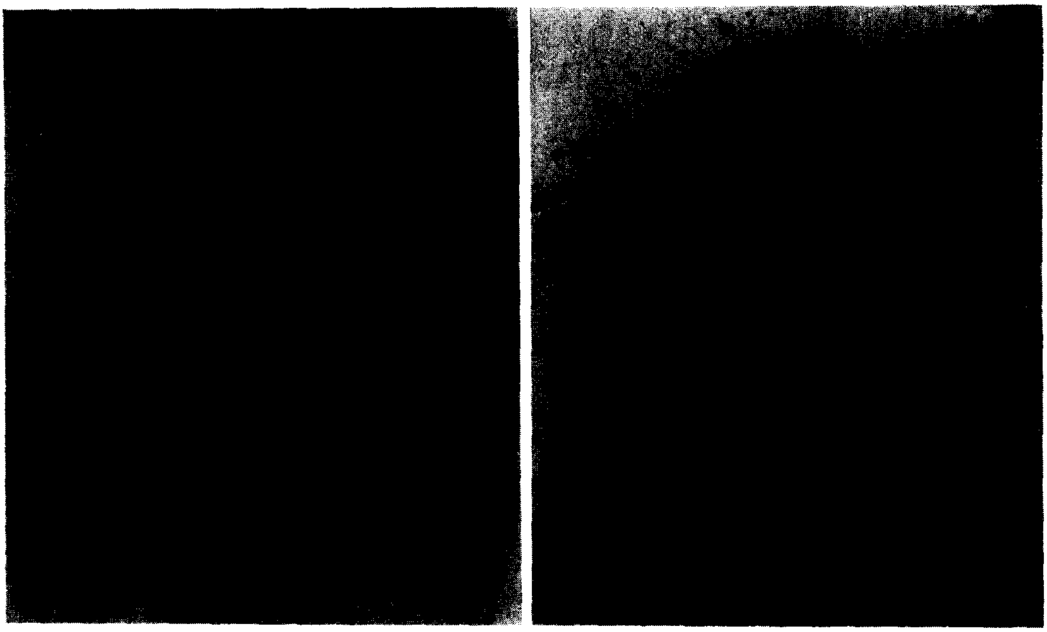
Note that the term κ, defined as the ratio of the reactor volume to the volumetric flow rate of the hydrogen purge stream, is a time constant which must be included in the conservation expression to account for the loss of poison by flow out of the reactor. Points were picked from the weight–history recordings and were fitted to Eq. (1) by a least-square method to derive the adsorption constant k'_a. The points and curves for three runs are shown in Fig. 4. Although the fit is respectable, it is not offered as experimental *proof* of a first-order adsorption process. The purpose here is rather to obtain a measure of the rate of the adsorption process. The rate constant for adsorption decreased with increased amount of poison, suggesting a possible correlation between the kinetic and adsorption rate constants. The kinetic rate constant evaluated at each degree of poisoning was plotted as a function of the following adsorption rate constant in Fig. 5. The approximately linear correlation is evidence for the contention that the area for reaction is proportional to or the same as that for the adsorption of poison. This could mean that arsine will adsorb only on platinum and not on arsine (probably converted to $PtAs_2$), or that the poison decreases (sinters) the surface area. However, BET surface area measurements showed the final surface roughness factor to be 1.4 compared to an initial value of 10. Therefore, the latter interpretation is favored.

Portions of poisoned and unpoisoned films were examined with a metallurgical microscope and representative micrographs are shown in Fig. 6. The inside of the film corresponds to the concave surface when it rolls up without assistance. Replicas of the film surface structure were examined with an electron microscope and the micrographs are shown in Fig. 7.

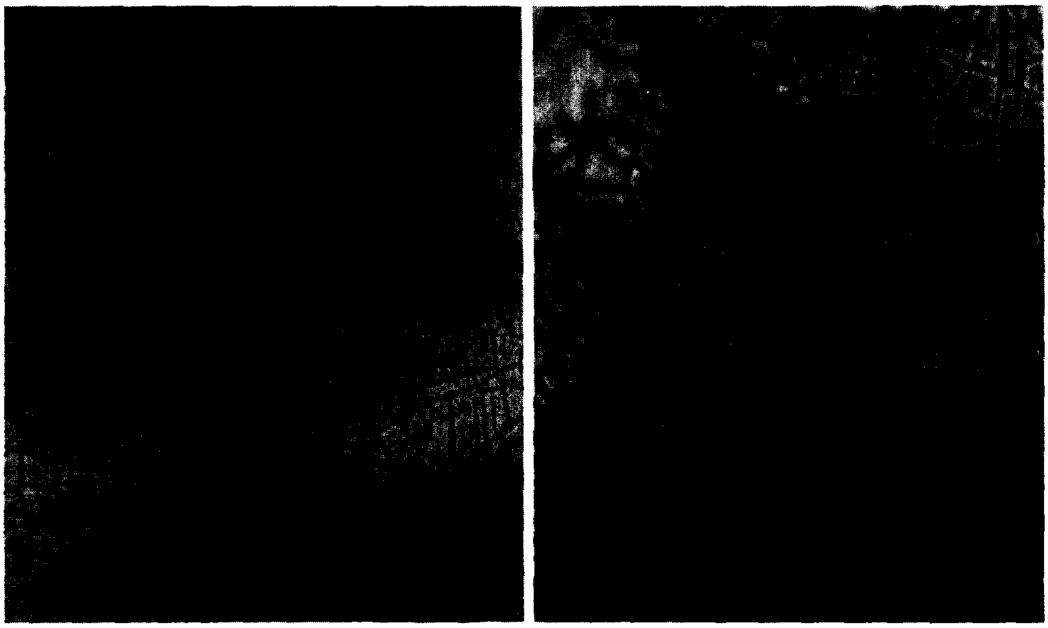
The micrographs of Fig. 6 show a mud-flat type cracking of the poisoned film where the cracks are depressions. The unpoisoned film has a network of large cracks on one side which can be distinguished from the poisoned film by their large size. The dark spots appear to be pieces of platinum that are much larger than the small crystals that make up the sponge-like coating. The electron micrographs of Fig. 7 show detail of the surfaces at much higher magnification. Uneven surface structure appears as darker areas accompanied by lighter areas from the shadowing of the replicas. The cracks in the platinum coating are also evident on the electron micrographs.

It is difficult to draw definite conclusions from the micrographs. The cracks appear to be a result of shrinking or sintering of the platinum coating which could result in a loss of the internal surface area of the sponge-like coating. However, the microstructure could not be seen to verify the apparent sintering because the crystals of the Pd–Au shadowing material masked the small crystals that made up the sponge-like platinum coating.

Other investigators (*25*) have shown that

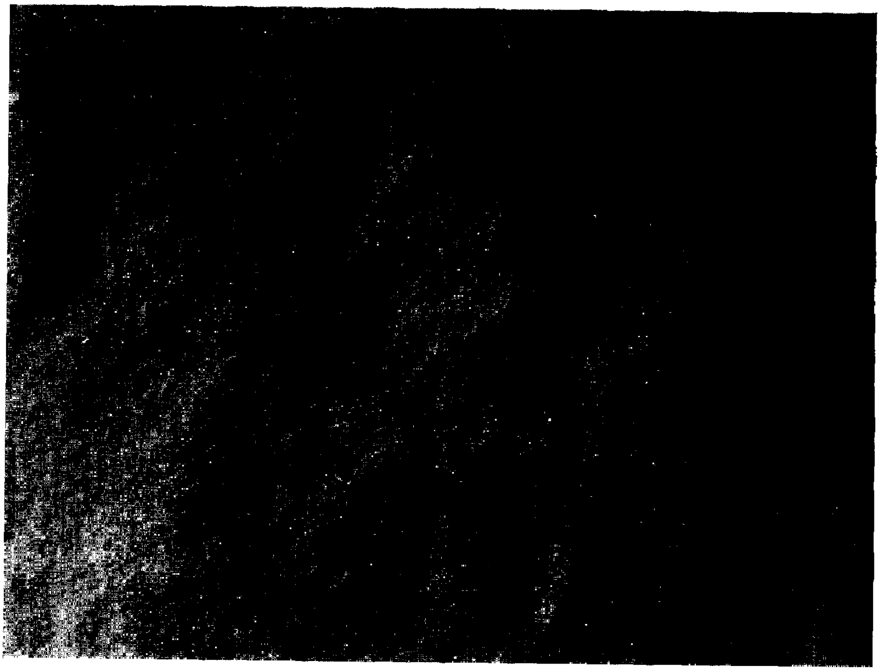


A. Outside X400 **B. Inside X400**



C. Outside X400 **D. Inside X400**

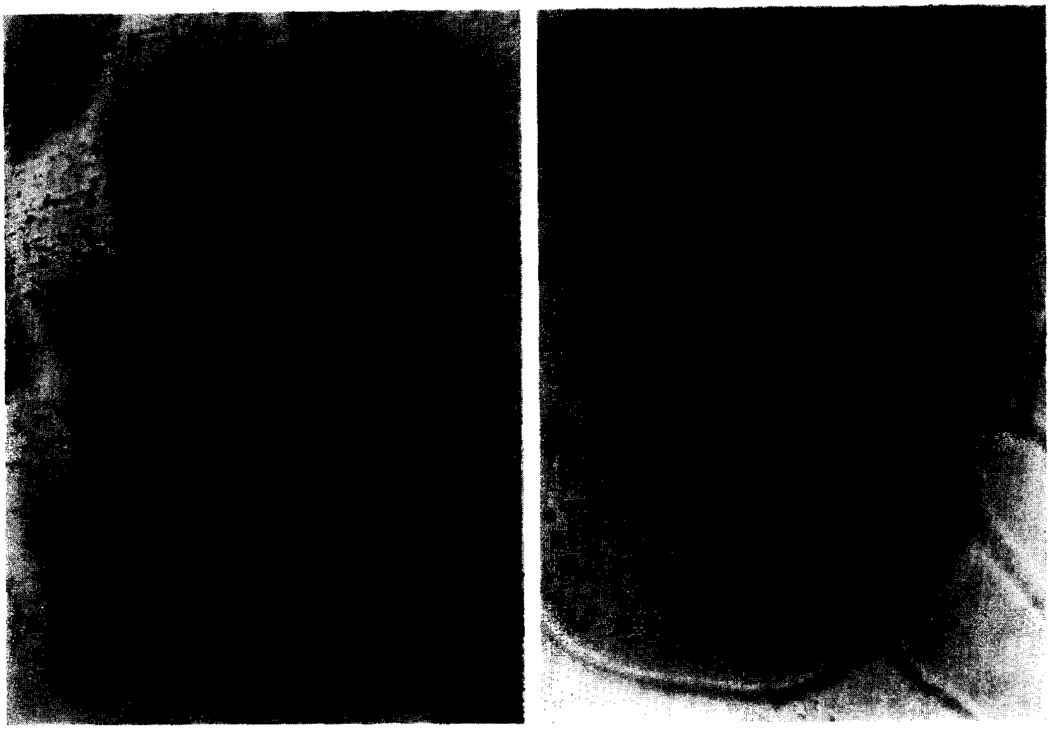
FIG. 6. Photomicrographs of platinum films: A and B, unpoisoned; C and D, poisoned.



A. Inside X24,000

B. Inside X20,000

FIG. 7. Photomicrograph of two-stage carbon replicas of the surface of platinum films; A, unpoisoned; B, poisoned.



A. Outside X400 **B. Inside X400**

FIG. 8. Photomicrographs of an activated platinum film.

evaporated platinum films may lose surface area through crystal growth as a function of heating and exposure to various gases. The platinum films used in this investigation were subjected to two conditions, other than poisoning, that could possibly lead to sintering; first, catalyst activation, and second, a kinetic run. Therefore, a portion of an activated film was examined with the metallurgical microscope. The micrographs in Fig. 8 show that some cracks develop in the surface as a result of activation; however, they are not as extensive and they do not cause sintering of the surface. Inasmuch as the films maintained a constant activity over a long period of time, the kinetic runs were not responsible for the sintering. The available evidence therefore supports the view that poisoning with arsine causes the catalyst to sinter.

The activation energies of the platinum film as the poisoning progressed were determined from the Arrhenius plots shown in Fig. 9. The numbers refer to the dose of poison given to the catalyst before the corresponding data were taken. The measured activation energies varied from 3.0 to 4.0 kcal/gmole-°K and the lack of a systematic variation in the activation energy indicates that the platinum surface was approximately uniformly active. This observation is consistent with the conclusions of other investigators (*25, 26*), who found that, with respect to the hydrogenolysis of cyclopropane over platinum, all forms of platinum are equally active; e.g., impregnated, foil, sintered, and unsintered platinum black.

The low values of the activation energy and the curvature in the Arrhenius plots were unexpected. The values of the activation energy reported by other investigators (*15–24*) using platinum catalysts range from 8.0 to 12.2 kcal/gmole-°K. The curvature in the Arrhenius plot might be caused by the adsorption of water at the low temperature (*27*). The weight of the catalyst always increased at the low temperature.

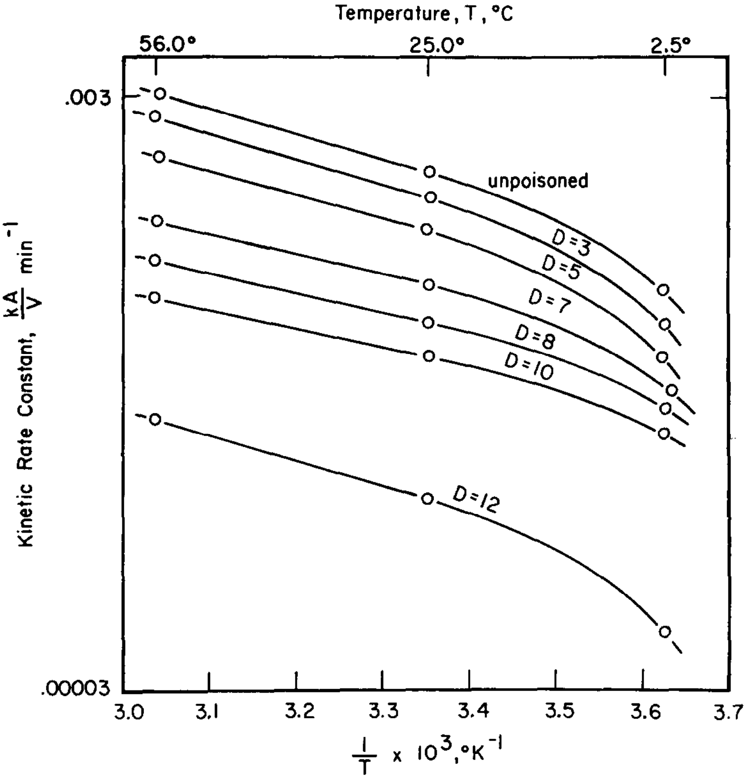


FIG. 9. Kinetic rate constants for a progressively poisoned film.

The curvature of the Arrhenius plot could not be explained (*32*) by diffusion influence, however this curvature might be caused by adsorption of water at the low temperature (*27*). The apparent weight of the catalyst always increased at low temperatures.

DISCUSSION

The results in Fig. 3 show that the activity of an evaporated-film platinum catalyst decreased approximately linearly with the weight of adsorbed arsine, and after adsorption of 747 μg of arsine the catalyst lost 86% of its surface. Activation treatments and extensive catalytic use did not decrease the catalytic activity of the platinum films. These observations were interpreted to mean that the loss in catalyst activity was due to a loss in surface area.

The correlation between the kinetic and adsorption rate constants (Fig. 5) indicates that the area for reaction is approximately proportional to or the same as that for the adsorption of poison. However, only 14% of the original surface area was available to either process as this work ended. Since the area was approximately uniformly active throughout the poisoning (Fig. 9) and activity decreased linearly with poisoning, it is not unreasonable to conclude that the surface area decreases approximately linearly with poisoning. Thus the group kA/V of Fig. 3 appears to decrease with poisoning because A decreases and k, the intrinsic rate constant, remains constant throughout the poisoning process.

A possible explanation will be discussed as to why arsine sinters the platinum film. Then, a simple poisoning model will be proposed which leads to a relationship between catalytic activity and surface area which fits the experimental data.

The evaporated catalyst surface remains thermally stable to the reaction in the absence of arsine because it was formed at a temperature higher than was used in the kinetic runs. What then is the interaction between arsine and the platinum surface?

Maxted and Ball (*3*) report that arsine on platinum "readily decomposes into a nondesorbable form." Wells (*28*) observed that after a small part of a platinum foil had reacted with arsenic to form $PtAs_2$, the foil melted at temperatures far below the melting point of platinum. The latter observation was made at temperatures much higher than used in the present experiment. However, it was found in this work that platinum black pellets sintered at 25°C without the influence of arsine when used as a catalyst for this reaction.

Therefore it seems reasonable to believe that arsine changed the properties of an otherwise thermally stable catalyst to cause it to sinter by lowering the temperature of thermal stability for the evaporated catalyst. Moreover, the mechanism of sintering strongly suggests the formation of $PtAs_2$ because of Wells' observation and because the 747 μg of arsine adsorbed corresponds to about three-fourths of a monolayer of $PtAs_2$ on the original catalyst surface. Unfortunately, direct observation of the sintering from the electron micrographs was not possible because the microcrystals of the platinum film were masked by the 100 Å crystals of the Au–Pd shadowing material on the carbon replicas of the film surface.

It is valuable to consider how sintering may happen. A possible answer is a combination of lattice strain and released energy associated with the adsorption of arsine. Ababurov and Grigorovich (*29*) used X-ray analysis to show that platinum catalysts poisoned with As_2O_3 in an oxidizing atmosphere have a small change in the crystal unit cell dimension. Platinum arsenide, formed from the adsorption of arsine, would have a greater tendency to change the crystal structure (because of the larger bulk of the molecule) than that observed by Ababurov and Grigorovich. The lattice parameter for $PtAs_2$ is 5.29 Å compared to 3.89 Å for platinum (*30*). The enthalpy of decomposition of arsine is $\Delta H_{298} = -43.49$ kcal/gmole (*31*). The enthalpy of formation for $PtAs_2$ is not known, but it is believed to be an exothermic reaction because $PtAs_2$ is a naturally occurring platinum ore (known as Sperrylite). That makes the enthalpy for the overall reaction

$$Pt + 2AsH_3 \rightarrow PtAs_2 + 3H_2,$$

greater than 90 and probably at least 120 kcal/gmole of Pt. The combination of significant lattice strain and released energy associated with the adsorption of arsine may well cause the surface to sinter as it is poisoned. This tends to support the inference of an approximately linear change in surface area with sintering.

It is significant to mention also that Maxted and Ball (*3*) were unable to regenerate platinum catalysts poisoned with arsenic using methods which were successful for regenerating Group VIII metals catalysts poisoned with other species. Such irreversibility is inherent in the interpretation of the present work.

In review, the significant results of this study are: The activity of the platinum film decreased approximately linearly with weight of adsorbed arsine; a linear correlation between the adsorption and kinetic rate constants was found which indicates that the area for reaction is proportional to or the same as that for the adsorption of arsine; and the catalyst lost 86% of its surface area during the poisoning process. These results are interpreted to mean that loss in catalytic activity is due to loss in surface area and the poisoning process is irreversible.

A simple model is consistent with these facts. Consider a unit of surface area of the platinum film as shown in Fig. 10. When some fraction, ϕ, of the unit surface is treated with arsine, $PtAs_2$ is assumed to form and sintering follows to decrease the area ϕ to a value ϵ. Hence part D of Fig. 10 is lost to the bulk. If $PtAs_2$ is assumed to form, then the poisoned area ϵ remaining must be divided into active, i.e., platinum metal surface and inactive areas ($PtAs_2$) because the arsine treatment is in a ratio of 3 arsine atoms to 2 platinum surface atoms (*32*). Accordingly a fraction $f\epsilon$ is active and $(1 - f)\epsilon$ is inactive. The quantity σ, defined as $\sigma = \epsilon/\phi$, can be approximated experimentally as the ratio of the final and original surface roughness factors which is 0.14.

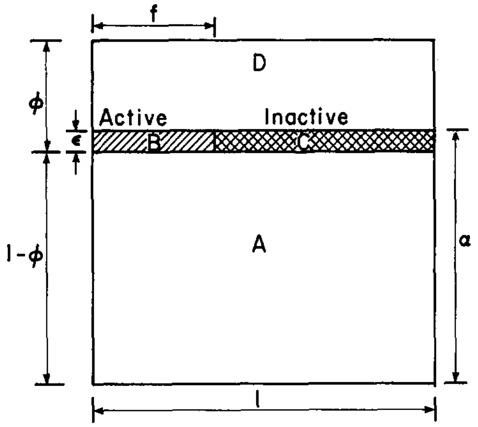


FIG. 10. Simple model for poisoning.

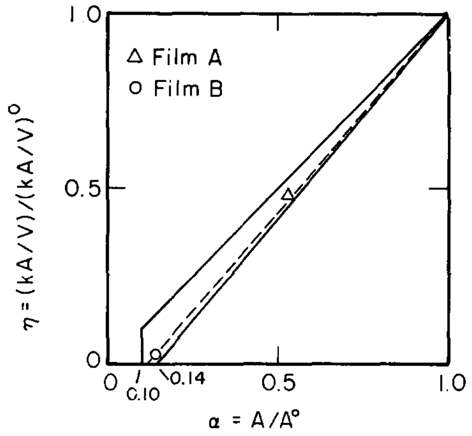


FIG. 11. Normalized kinetic rate constant, k', as a function of normalized area for poisoned films.

According to this model, then, the fraction of the original activity remaining is equal to A + B or $1 - \phi + f\epsilon$ and the fraction of the original surface area remaining, α, is A + B + C or $1 - \phi + \epsilon$. These relationships can be combined with $\sigma = \epsilon/\phi$ to give the desired linear relationship between catalyst activity and surface areas.

$$\eta = 1 - (1 - \alpha)\left(\frac{1 - f\sigma}{1 - \sigma}\right). \qquad (2)$$

Two limits can be imposed on this model, and they are shown in Fig. 11. The sintered portion of the platinum film (film B) could be totally active, $f = 1.0$. Then $\eta = \alpha$. However, there is a geometric limit to α and that limit is 0.1 since its original surface roughness factor is 10. After the platinum film has been completely sintered, the remaining area is then poisoned (represented by the vertical line at 0.10). The other limit is that the sintered portion may be totally inactive, $f = 0$. For this case,

$$\eta = \frac{\alpha - \sigma}{1 - \sigma}. \qquad (3)$$

In addition, the roughness factor may be greater than unity after poisoning (it was 1.4 for film B). This limit is shown by the solid line drawn between $\alpha = 0.14$ and $\alpha = 1.0$.

The proposed relationship between catalyst activity and surface area is shown graphically in Fig. 11. The two data points represent the final conditions of films A and B. Film A was deposited and poisoned using procedures identical to those used for film B and should, therefore, give results consistent with those for film B. The broken line is for values of $f = 0.25$ and $\sigma = 0.14$. The value of 0.25 was chosen for f because the quantity of arsine adsorbed by the catalyst is enough to effect a 75% conversion of the original platinum surface atoms. However, the limits of the model as shown in Fig. 11 are narrow enough that almost any value of f would be acceptable. It should also be noted that while extensive data are not available, all of the data pertaining to the proposed model are consistent with it.

Most poisoning studies (*1–14*) have been made using a strongly chemisorbed species as the poison. A notable exception among reported losses in catalytic activity involves agglomeration of finely dispersed metals on supports. In the first case, loss in activity is normally related to fractional coverage of the catalyst surface or active sites with the poison. When poisoning results in the formation of a chemical compound, it is more meaningful to relate activity to conversion of the surface instead of equivalent monolayers. The present work is a good example. The ratio of adsorbed arsine molecules to the original number of surface platinum atoms is 3:2. Since $PtAs_2$ is apparently formed, or arsine is adsorbed in the atomic ratio of 2:1, enough arsine was adsorbed to convert

75% of the original surface atoms to $PtAs_2$. The significance of either measure is diminished because many of the original surface platinum atoms appear to end up in the bulk as platinum arsenide.

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