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Selective Poisoning of H_2–D_2 Equilibration on Transition Metals by Carbon Monoxide

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Hall and co-workers used CO_2 poisoning to determine the upper bounds for active site densities in hydrogen equilibration and *o–p* hydrogen conversion on alumina. This concept is generalized to the use of strongly adsorbed poisons to provide mechanistic interpretations for hydrogen equilibration over group VIII transition metals. Using known coverages of preadsorbed CO as a specific poison on polycrystalline Pt and Rh wires, hydrogen equilibration rates (293–400°K, 0.5 Torr) were measured and compared to the equilibration rates in the absence of CO, after cleaning in ultrahigh vacuum (10^{-8} Torr). It was concluded that (i) the hydrogen equilibration reaction required a dual-site mechanism showing dissociative chemisorption to be the rate-determining step, (ii) the Pt and Rh surfaces were uniformly active, and (iii) the upper bound to the number of active sites was $\sim 10^{15}/cm^2$, or every surface metal atom. Hydrogen equilibration is a *facile* reaction for these experimental conditions but the reaction may become demanding under conditions where the surface coverage by adsorbed hydrogen is small (<0.2 monolayer). Other surface reactions, such as the electrocatalytic hydrogen molecule oxidation on Pt poisoned by CO and CO_2^{2-} (reduced carbon dioxide), show nearly identical results.

INTRODUCTION

The study of hydrogen[1] equilibration over supported Pt by Poltorak and Boronin (*1, 2*) indicated that this reaction should be termed a *facile* reaction in the classification of reactions by Boudart *et al.* (*3*). Such reactions are insensitive to the mode of catalyst preparation, have every surface metal atom as an active site, and are insensitive to the size of catalyst crystallites. Recent investigations have raised some questions as to the appropriateness of this classification. A dependence of equilibration rate on pretreatment of Pt wire (*4*), on the density of (100) steps in a (111) Pt single crystal (*5*), and the observation of intrinsic heterogeneity for hydrogen adsorbed on Pt (*6, 7*) indicate that this reaction may not be a *facile* reaction in the general sense.

It is the purpose of this work to examine the relationships of intrinsic or induced heterogeneities in Pt and Rh metal surfaces to the activities of the metal surfaces for hydrogen equilibration and to obtain a measure of the number of active sites for this reaction. Hall and his co-workers (*8, 9*) pioneered the use of CO_2 poisoning to measure the site density on alumina, and the heterogeneity of the alumina surface, for hydrogen equilibration. This technique is applied in this work to transition metals, with carbon monoxide as the poison. To use the technique successfully, the poison must have special adsorptive properties. It must be so strongly adsorbed that there is no displacement of the poison from the surface by reactant species, nor any chemical reaction between the adsorbed poison and reactant surface species. A one-to-one correspondence between an adsorbed poison

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[1] Both H_2 and D_2 will be referred to throughout this work as "hydrogen" in discussing H_2–D_2 equilibration.

molecule and a reactant adsorption site and similar distributions in energies of adsorption for both poison and reactant molecules are required. Carbon monoxide is strongly chemisorbed on both Pt and Rh, is not displaced from the surface by hydrogen, does not react with hydrogen below 200°C (*10*), and the CO/H stoichiometry is nearly 1/1 (*10, 11*). Hydrogen and carbon monoxide have similar distributions of the energies of adsorption on the surfaces of Pt and Rh, as shown by TPD curves and the variations in the heats of adsorption with coverage (*12–16*). Poisoning of the Pt and Rh surfaces by carbon monoxide can, therefore, be used to investigate the effect of surface heterogeneity on catalytic activity, and to titrate the surface for the site density. Knowledge of these factors is requisite for the proper classification for the hydrogen equilibration reaction.

EXPERIMENTAL

Catalysts

Englehard Pt black was used for the measurements of carbon monoxide and hydrogen coverages on Pt. The Pt black had an initial BET surface area of 27 m^2/g. In order to assure a constant surface area during the adsorption experiments, the catalyst was presintered by heating in flowing H_2 at 250°C for 4 hr. The BET area dropped to 5.5 m^2/g. The catalyst was again sintered in H_2 at 250°C for an additional 2 hr, and the BET area had leveled out at 3.8 m^2/g. Rh black was found to be unsuitable for accurate adsorption experiments because of nearly continuous sintering at 150–250°C in H_2. Instead, a Rh supported on graphitized carbon black catalyst was used. Conventional impregnation techniques were used with the appropriate amount of $RhCl_3$ in aqueous solution to give a 17.5% Rh. The supported Rh was reduced and presintered in flowing H_2 for 4 hr at 250°C. The Rh content of the catalyst was measured by atomic adsorption spectroscopy. X-ray diffraction studies of this material indicated an average crystallite size of 75 Å (64 m^2/g).

H_2–D_2 equilibration experiments were carried out on polycrystalline Pt and Rh wire from Englehard.

Gases

Both hydrogen (Matheson CP grade) and carbon monoxide (Linde CP grade) used for gas-phase chemisorption measurements were purified by passage through 0.5% Pd on asbestos catalyst at 350°C, followed by a trap containing zeolite at −195°C.

For H_2–D_2 equilibration experiments, hydrogen (Precision Gas Products Ultra-High Purity Grade) and deuterium (Precision Gas Products Research Grade) were used after passage through a liquid nitrogen trap; carbon monoxide (Precision Gas Products Research Grade) was used without further purification.

Gas-Phase Adsorption

A conventional glass BET volumetric apparatus equipped with a Hg diffusion pump capable of a vacuum of 1×10^{-6} Torr was used.

The pretreatment in most experiments was reduction in H_2 at 200°C for 2 hr, followed by evacuation at 200°C and 10^{-6} Torr for 2 hr. The number of sites for hydrogen chemisorption was obtained by measuring the volume of hydrogen adsorbed at 25°C and at gas pressures of 40–300 Torr. There was no significant adsorption of hydrogen on the carbon support, and there was no evidence of hydrogen spillover in the Rh–carbon system, as the surface area calculated from the hydrogen adsorption agreed closely with the value indicated by the X-ray diffraction. The adsorption was very rapid and equilibrium was reached in less than 10 min.

Hydrogen chemisorption was poisoned by preadsorbing carbon monoxide to a measured pressure at temperatures from 100 to 200°C for 30 min. The nonadsorbed, excess carbon monoxide was pumped out and the temperature adjusted to 25°C. It was confirmed in separate experiments with the mass spectrometer that no carbon monoxide was desorbed from the surface of either Pt or Rh during the pump-out and temperature adjustment. The hydrogen chemisorption was then carried out at the baseline temperature and hydrogen gas pressures, and the number of unpoisoned hydrogen chemisorption sites obtained.

Chemisorbed carbon monoxide was completely removed by oxidation with 300 Torr oxygen for several minutes, followed by outgassing and the standard reduction pretreatment.

H_2–D_2 Equilibration

The apparatus for measuring H_2–D_2 equilibration rates was a static reactor system similar to that of Breakspeare *et al.* (*4*). The reactor, gas mixing, and sampling system were constructed entirely from Pyrex. H_2, D_2, and HD concentrations were measured with a CEC Mass Spectrometer, Model 21-614. A cylindrical Pyrex tube reactor containing the wire catalyst was connected to the vacuum manifold and a gas mixture bulb via a magnetically operated ground glass dekker valve with an intervening liquid N_2 trap, and to the mass-spectrometer sampling system by a 3-ft length of 250-μm Pyrex capillary. Gases were separately metered into the system with partial pressures monitored by a calibrated pirani gauge. Sampling from the reactor was continuous and at constant pressure, with the rate adjusted by a micrometer-calibrated fine metering value. Experiments carried out in an empty reactor confirmed there was no exchange in the gas handling system or on the walls of the mass spectrometer.

Prior to sealing the wire catalyst in the reactor tube, the wire was cleaned electrochemically by potential cycling, dipped into boiling nitric acid, washed in triply distilled water, and sealed into the reactor tube. The reaction system (ionization gauge, dekker value, reactor tube) could be baked out at 523°K to give, after cooling, a residual pressure of 5×10^{-8} Torr.

To measure the equilibration rates for clean Pt and Rh, a cycle of treatments in 1 Torr oxygen at 773–973°K followed by reduction in 2 Torr hydrogen at 773°K and by outgassing at 773°K was used. The H_2–D_2 reaction was carried out batchwise, by admitting a stoichiometric mixture to the reactor and closing the dekker value. Time zero was established by appearance of D_2 in the mass spectrometer. To observe the H_2–D_2 equilibration rate on a poisoned Pt or Rh surface, an accurately metered pressure of carbon monoxide was admitted to the reactor, the nonadsorbed carbon monoxide pumped out, and the stoichiometric mixture of H_2–D_2 admitted to start the reaction. All poisoning experiments were carried out at total (H_2–D_2) pressures of 0.5 Torr and temperatures from 273 to 473°K. Following the pumping out of nonadsorbed carbon monoxide, no carbon monoxide could be observed in the mass spectrometer, nor could any reaction products of hydrogen and carbon monoxide (methane, methanol, formaldehyde, etc.) be observed in the short time period for equilibration (less than 10 min).

Analysis of Equilibration Reaction Kinetics

Due to a residual background of hydrogen in the mass spectrometer, the time progress of the reaction was monitored from the relative heights of the HD and D_2 peaks. Let y be the conversion at time t, y_e the conversion at equilibrium. If R = (height of D_2 peak)/(height of HD peak) $= P_{D_2}/P_{HD}$, then $y = 1/(2R + 1)$. The sampling rate was adjusted so that over the time course of the reaction to equilibrium the total pressure changed less than 10%. If both the forward and reverse reactions follow first-order rate laws, then, for constant total pressure,

$$y/y_e = (1 - e^{-kt}), \tag{1}$$

where k (min^{-1}) relates the rate to the distance from equilibrium. It was found that for pressures 0.5–10 Torr and temperatures 295–473°K, plots of $\ln[1 - y/y_e]$ vs t yielded straight lines, with slopes $-k$. The absolute rate defined by Eley (*12*) is k_m (molecules $\mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$), where

$$k_m = \frac{Nk}{60A}, \tag{2}$$

N is the number of molecules in the reactor, and A is the area of the wire.

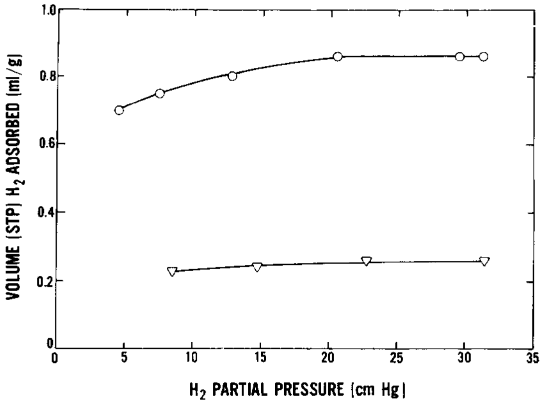

FIG. 1. Poisoning of hydrogen chemisorption on Pt by preadsorbed carbon monoxide. Hydrogen adsorption at 25°C: (○) clean Pt, (▽) following adsorption of 2 Torr CO at 175°C.

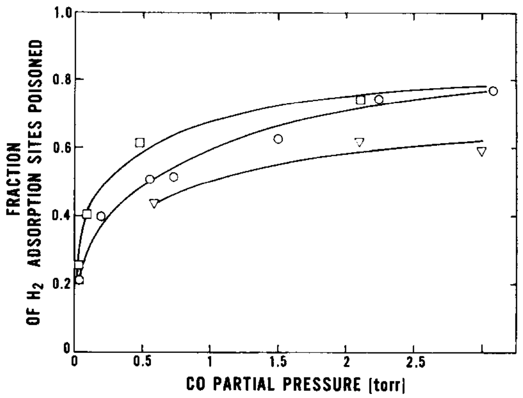

FIG. 3. Fraction of hydrogen chemisorption sites on Pt poisoned as a function of carbon monoxide pressure for (□) 110°C, (○) 150°C, (▽) 190°C.

RESULTS

Poisoning of H_2 Chemisorption

Isotherms for chemisorption of hydrogen on Pt and Rh are shown in Figs. 1 and 2. The volume of hydrogen chemisorbed on unpoisoned Pt and Rh is exactly what was expected from the BET and X-ray diffraction results, respectively (4 and 64 m^2/g based on 1.12 × 10^{15} H atoms cm^{-2}). When carbon monoxide was preadsorbed on the catalyst surface, the hydrogen chemisorption was uniformly reduced at every hydrogen partial pressure. If the fraction of hydrogen chemisorption sites removed by carbon monoxide poisoning is denoted θ_{CO}, then

$$\theta_{\mathrm{CO}} = 1 - (v_{\mathrm{CO}}/v), \qquad (3)$$

where v is the volume of hydrogen chemisorbed on the clean surface and v_{CO} is the volume of hydrogen chemisorbed on the carbon monoxide-poisoned surface. The θ_{CO} values are shown in Figs. 3 and 4 as a function of the temperature and carbon monoxide partial pressure. The maximum amount of hydrogen sites poisoned by carbon monoxide was found to be greater for Rh than for Pt, and the Rh surface was poisoned

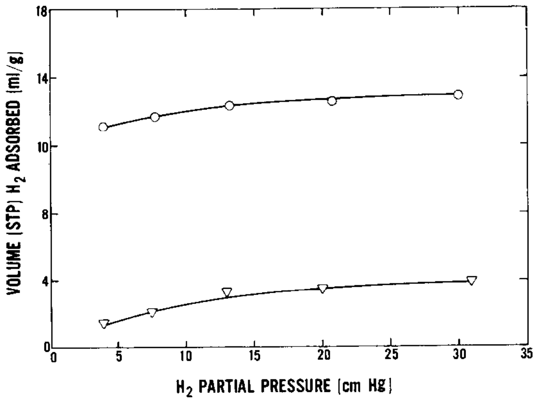

FIG. 2. Poisoning of hydrogen chemisorption on Rh by preadsorbed carbon monoxide. Hydrogen adsorption at 25°C: (○) clean Rh, (▽) following adsorption of 0.3 Torr CO at 150°C.

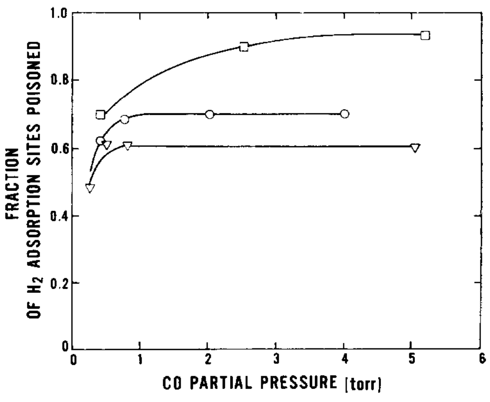

FIG. 4. Fraction of hydrogen chemisorption sites on Rh poisoned as a function of carbon monoxide pressure: (□) 25°C, (○) 150°C, (▽) 190°C.

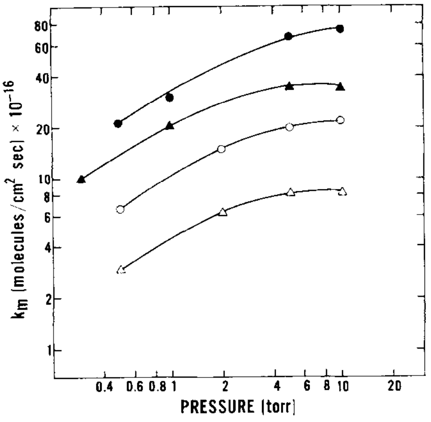

FIG. 5. Hydrogen equilibration on unpoisoned Pt and Rh surfaces: (○) Pt at 25°C, (△) Rh at 25°C, (●) Pt at 150°C, (▲) Rh at 150°C.

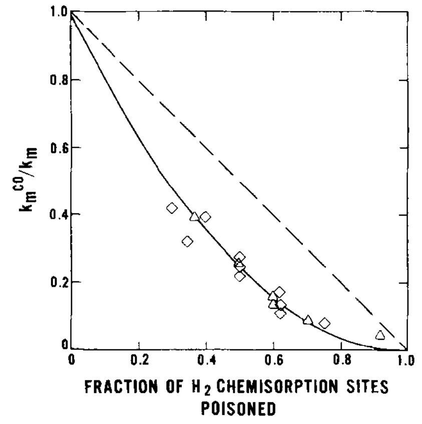

FIG. 7. Poisoning of the rate of equilibration, k_m, on (◇) Pt and (△) Rh by adsorbed carbon monoxide. Solid line is $(1 - \theta_{CO})^2$ vs θ_{CO}, where θ_{CO} is the fraction of H_2 chemisorption sites poisoned.

at lower carbon monoxide pressures than those required to achieve the same level of poisoning on Pt.

H_2-D_2 Equilibration

(i) Unpoisoned Pt and Rh. The kinetic properties of Pt and Rh for hydrogen equilibration were nearly identical. The absolute rates of equilibration are shown in Fig. 5 for hydrogen pressures of 0.3–10 Torr. The order of reaction at 0.3–0.6 Torr was approximately 0.5, and the order decreased as the pressure increased, approaching zero order at 10 Torr. The orders of reaction did not change significantly with temperature in the range 295–473°K. The nearly zero-order activation energy determined from the Arrhenius plot of Fig. 6 was 2.5–3 kcal/mole for both Pt and Rh. The k_m values for Pt found in this work are very similar to the previously reported results of Breakspeare *et al.* (*4*) for the same conditions of temperature and partial pressure (273°K, 0.4 Torr, $\log k_m = 17.646$).

(ii) CO-poisoned equilibration. It was found that the results of H_2–D_2 equilibration over both Pt and Rh poisoned by

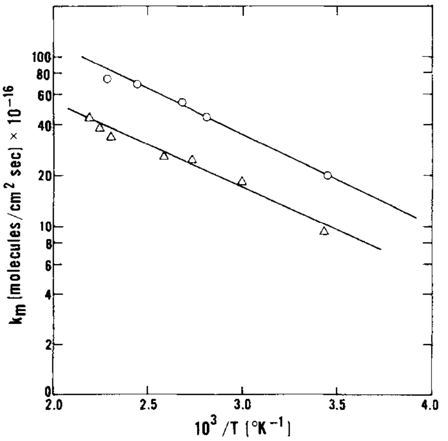

FIG. 6. Arrhenius plot for hydrogen equilibration on unpoisoned (○) Pt and (△) Rh at 10 Torr pressure.

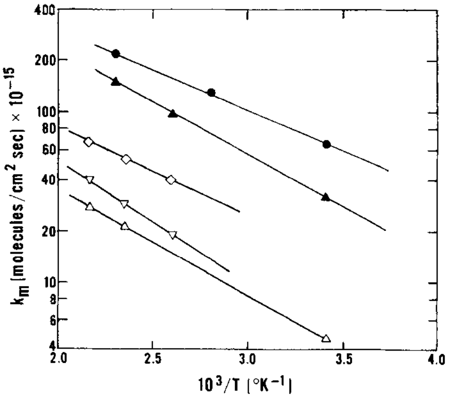

FIG. 8. Arrhenius plot for unpoisoned (●) Pt and (▲) Rh and for poisoned Pt, (◇) $\theta_{CO} = 0.50$, (▽) $\theta_{CO} = 0.62$, and Rh, (△) $\theta_{CO} = 0.60$.

carbon monoxide could be reduced to a single correlation with θ_{CO}, the fraction of hydrogen chemisorption sites poisoned by carbon monoxide. Figure 7 shows the correlation of the ratio of k_m^{CO}, the rate of equilibration on a CO-poisoned surface at a given temperature to k_m, the rate on the unpoisoned surface at the same temperature. At a given coverage, variation in the exchange temperature did not change the k_m^{CO}/k_m ratio significantly, indicating the activation energy on poisoned and unpoisoned surfaces was essentially the same. The temperature dependence of the equilibration rate at different extents of poisoning is shown in Fig. 8. The activation energy on the available sites remained constant at about 3 kcal/mole.

DISCUSSION

Surface Heterogeneity

There is little doubt that the surface of Pt and Rh is heterogeneous for hydrogen chemisorption, as indicated by flash desorption (*6*) and field emission (*14*) experiments. Flash desorption of carbon monoxide from Pt indicated (*15, 16*) a similar heterogeneity and a similar sequential formation of the tightly bound species at low coverage with progressively weaker bound species at higher coverages. It seems likely that the hydrogen chemisorption sites with the highest heat of adsorption are poisoned first, followed by sites with successively higher heats of adsorption as the carbon monoxide coverage increases. This would be expected to give rise to an activation energy which changed with poisoning of the surface. This was not observed to be the case, and it would appear that the surface is uniformly active for hydrogen equilibration.

The solid line through the data of Fig. 7 is just the function $(1 - \theta_{CO})^2$ vs θ_{CO}. This function is what one would expect for dissociative (dual-site) mechanism on a uniform surface. The recent works of Breakspeare *et al.* (*4*) and Tsuchiya *et al.* (*6, 7*) of H_2–D_2 equilibration on Pt have indicated that the most likely high-temperature mechanism ($T > 200$°K) is the Bonhoeffer-Farkas sequence

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}D_2 + 2M \rightleftharpoons MHMD \rightleftharpoons HD + 2M.$$

Measurements of hydrogen atom diffusion rates (*14, 15*) across transition metal surfaces have indicated that the collision rate of adsorbed atoms at 400°K was 10^4 times greater than the rate of exchange at equivalent conditions. It is therefore unlikely that surface diffusion is limiting the equilibration rate at the temperatures of this work. The rate of equilibration for a uniformly active surface will then be given by either the rate of chemisorption,

$$k_m = k_a p(1 - \theta)^2, \tag{4}$$

where p is the partial pressure of hydrogen, or the rate of desorption

$$k_m = k_d\theta^2, \tag{5}$$

where θ is the fraction of the total available adsorption sites occupied. In the presence of carbon monoxide poisoning,

$$\theta = \theta_H^{CO} + \theta_{CO},$$

where θ_H^{CO} is the fraction of the total available sites occupied by adsorbed hydrogen. θ_H^{CO} and θ_{CO} are related by Eq. (3):

$$\theta_H^{CO} = (1 - \theta_{CO})\theta_H, \tag{6}$$

where θ_H is the fraction of the unpoisoned surface covered by adsorbed hydrogen at a given temperature and hydrogen pressure. Then the rate of equilibration over a carbon monoxide poisoned surface will be given by

$$k_m^{CO} = (1 - \theta_{CO})^2 k_a P(1 - \theta_H)^2$$

or

$$k_m^{CO} = (1 - \theta_{CO})^2 k_d \theta_H^2.$$

For either adsorption or desorption controlling, it is clear that the ratio of k_m on the poisoned surface to the k_m^{CO} on the unpoisoned surface will be just $(1 - \theta_{CO})^2$. This function fits the observed data extremely well, as Fig. 7 indicates, for both Pt and Rh.

From the results of selective poisoning of hydrogen chemisorption sites on Pt and Rh surfaces, it can be concluded that although the surfaces are heterogeneous in the sense of heats of adsorption that vary with coverage the surfaces are uniformly active for high-temperature H_2–D_2 equilibration. Some of the results of Van Cauwelaert and Hall (*8*) indicated this may also be true of H_2–D_2 equilibration on activated alumina. These investigations used selective poisoning of alumina by carbon dioxide and found that the activation energy for H_2–D_2 equilibration (273°K) was the same for both poisoned and unpoisoned surfaces and was independent of coverage by the poison. It may be that homogeneity is a general property of surfaces which catalyze H_2–D_2 equilibration through the dissociative mechanism (Bonhoeffer-Farkas). This uniformity, however, may also arise from the conditions at which equilibration reactions are usually carried out. These conditions are generally 1 Torr, or more, and temperatures from 273 to about 500°K. From the orders of reaction observed in this work, and those reported by Breakspeare *et al.* (*4*), the average hydrogen coverage of the metal surface during equilibration experiments on Pt or Rh at 1 Torr and 273–473°K varies from 0.5 to 1.0. During equilibration on the poisoned surface, at least 0.3 of the surface is covered by carbon monoxide, and half of the remaining unpoisoned sites are covered by adsorbed hydrogen, so that equilibration is actually catalyzed by only that portion of the surface characteristic of coverages from 0.65 to 1.0. In the region of coverage from 0.65 to 1.0 the heat of adsorption of either hydrogen or carbon monoxide does not change (*13*, *16*) greatly with coverage. Therefore, the conclusion that the surface of Pt and Rh is homogeneous with regards to high-temperature H_2–D_2 equilibration should be restricted to the experimental conditions of this work, 0.2–10 Torr, 273–473°K.

Facile Reactions

The absence of surface heterogeneity for the H_2–D_2 reaction on Pt implies that the activity should not be a function of Pt crystallite size. This agrees with the previous observations (*1*, *2*) that the activity of Pt for equilibration at 0.05 Torr and 293°K was not a function of Pt crystallite size. The selective poisoning results of Figs. 7 and 8 clearly indicate that the surface is titrated by poison only when θ_{CO}, the fraction of hydrogen adsorption sites poisoned, reaches unity, so that every Pt or Rh surface atom is an active site for H_2–D_2 equilibration, corresponding to a site density of $\sim 10^{15}$ cm^{-2}. Boudart *et al.* (*3*) described reactions which are insensitive to the mode of catalyst preparation and to the size of the catalyst crystallites as *facile* reactions. Such reactions depend only on the nature of the atoms of the surface, and a site density of $\sim 10^{15}$ cm^{-2} is expected. The uniformity of the Pt and Rh surface and the site densities measured for these surfaces meet in the most general way the classification of the high-temperature H_2–D_2 equilibration reaction as a *facile* reaction on Pt and Rh. Since all of the group $VIII_2$ and $VIII_3$ metals have very similar properties with regard to hydrogen activation and chemisorption, it may be that this classification for hydrogen equilibration can be extended to all the group $VIII_2$ and $VIII_3$ transition metals.

The Rate-Determining Step in Hydrogen Equilibration

The classification of hydrogen equilibration as a *facile* reaction would appear to be in conflict with the recent results of Bernasek *et al.* (*5*). The conflict arises because of the drastically different experimental conditions employed. In the latter work, equilibration was studied using a H_2–D_2 molecular beam and Pt (111) and stepped (111) single crystals, with an effective pressure of $\sim 10^{-8}$ Torr and temperatures from 300 to 1000°K. Isotopic exchange was observed only for the stepped surface, and led to the conclusion that hydrogen dissociation occurs only at the steps in the atomic surface. At these experimental conditions, the surface coverage by chemisorbed hydrogen would be less than 0.2 (*4*), a much lower hydrogen coverage than is present during equilibration experiments at higher pressures, and a totally different surface energy distribution is present at these lower coverages. The explanation of the results of Bernasek *et al.* (*5*) lies in the altered potential energy diagram at low hydrogen partial pressures.

The present work and previous work of

other investigators establishes with relative certainty the dissociative (Bonhoeffer-Farkas) mechanism for high-temperature equilibration on Pt. Using Eqs. (4) and (5) and assuming Langmuir adsorption, the true activation energy for hydrogen chemisorption and for desorption can be calculated from the apparent activation energy and the heat of adsorption, λ.

$$E_{\mathrm{app}} = RT^2 d(\ln k_m)/dT \qquad (7)$$

and

$$E_a = E_{\mathrm{app}} - \lambda\theta \qquad (8)$$

$$E_d = E_{\mathrm{app}} + (1 - \theta)\lambda. \qquad (9)$$

From the pressure dependence of k_m in Fig. 5 the coverage of the Pt and Rh surfaces by chemisorbed hydrogen can be estimated as 0.5–1.0. In this region of coverage, the heat of adsorption is approximately (*12, 13*) 7.5 kcal/mole. From the temperature dependence of k_m observed in this and other work (*4, 7*), the true activation energy for chemisorption is essentially zero, and the true desorption activation energy is 4–8 kcal/mole. The corresponding potential energy diagram for hydrogen chemisorption is shown in Fig. 9, which applies to the energetics of hydrogen equilibration at higher coverage. Since the true activation energy for chemisorption cannot be lower than it already is at high coverage, the shape of the potential energy diagram at low coverage, where λ increases rapidly to 32 kcal/mole (*13*), is easily envisaged. At high hydrogen coverages on Pt and Rh surfaces, desorption from the surface takes place from the low-energy chemisorption sites and adsorption takes place uniformly on any pair of unoccupied sites. As the coverage is lowered, the heat of adsorption increases from ~5 to ~10 kcal/mole at half a monolayer. According to the poisoning results of this work, the variation in the heat of adsorption changes the activation energy by a negligible amount (less than 1 kcal/mole). This implies either (i) the Brønsted exponent for hydrogen chemisorption is very small (0.1–0.2) or (ii) desorption occurs preferentially from the low-energy sites with rapid diffusion across the surface from the high-energy sites. The latter possibility seems more likely. As the coverage of the surface decreases below half a monolayer, the diffusion rate (flux) across the surface may diminish to the point where both the surface diffusion and desorption from high-energy sites are rate controlling. The apparent activation energy will drop to essentially zero, since as $\theta \rightarrow 0$, $E_d \rightarrow \lambda$ and $E_{\mathrm{app}} \rightarrow 0$ by Eq. (9). Such a transition in activation energy was observed by Breakspeare *et al.* (*4*) at $T >$ 500°K. The results of Bernasek *et al.* (*5*) can be interpreted as consistent with this picture of the energetics of hydrogen equilibration. At the very low coverages employed in their work, the surface diffusion to low-energy sites for desorption was probably rate controlling, these low-energy sites corresponding to steps in the atomic surface. On the (111) single crystal, the density of these steps is very much smaller than it is on the high-Miller-index terraced surface. Desorption from the high-energy chemisorption sites is the only alternative to diffusion to low-energy sites, and this alternative is very slow owing to the large (true) activation barrier for desorption at low coverage.

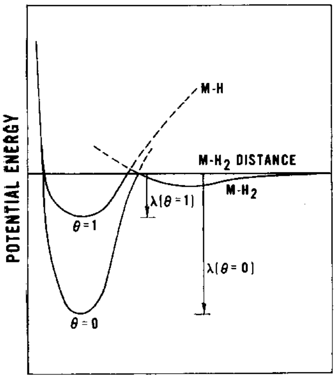

FIG. 9. Potential energy diagram for hydrogen chemisorption on a Pt or Rh surface. λ is the heat of adsorption, θ the coverage of the surface by adsorbed hydrogen.

Hydrogen desorption, therefore, from Pt, and possibly from other transition metal surfaces, is not a *facile* reaction in the general sense. Hydrogen dissociation on Pt and Rh is a *facile* reaction in the general sense. High-temperature ($T > 273°K$) hydrogen equilibration may be classified as a *facile* reaction when the experimental conditions are such that the surface coverage by chemisorbed hydrogen is high (0.5–1.0 monolayers) and may be termed a *demanding* reaction at conditions such that surface diffusion–desorption becomes rate controlling.

Generalization to Other Systems

The poisoning of electrochemical hydrogen oxidation in acid electrolyte by carbon monoxide and "reduced carbon dioxide" adsorbed on Pt indicates the surface chemistry for this system is very similar to that for the gas phase chemisorption of hydrogen. Figure 10 is a plot of the data of Stonehart and Kohlmayer (*17*) put into the form used for the analysis of hydrogen equilibration. The results for poisoning by carbon monoxide are close to the $(1 - \theta_{\text{poison}})^2$-vs-$\theta_{\text{poison}}$ line, indicative of a uniformly active surface for a two-site step, probably a hydrogen dissociation step. Since, it has been demonstrated recently (*18*) that the rate-determining step for hydrogen oxidation on Pt is the dissociative chemisorption step, this result is not entirely unexpected.

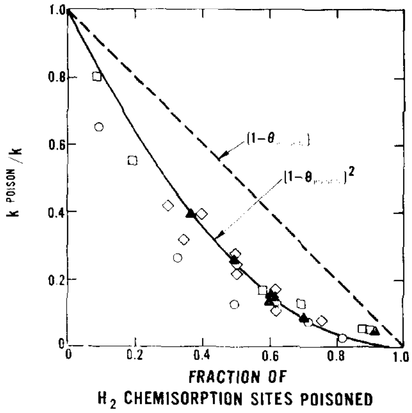

FIG. 10. Poisoning of electrochemical hydrogen molecule oxidation on Pt by (□) carbon monoxide and by (○) "reduced carbon dioxide" species. Poisoning of H_2-D_2 equilibration on (◇) Pt and (▲) Rh by adsorbed carbon monoxide.

"Reduced carbon dioxide" is a two-electron surface species produced by the reaction of CO_2 with chemisorbed hydrogen atoms (*19*) on the Pt surface. The exact configuration of the species is not known, but it is clearly a physically larger molecule than CO and one molecule may bridge two Pt sites. The poisoning of hydrogen oxidation by "reduced carbon dioxide" was in fact observed to be greater than that expected for the elimination of one active site per molecule, as indicated by the data falling below the $(1 - \theta_{\text{poison}})^2$-vs-$\theta_{\text{poison}}$ line.

These results on the poisoning of electrochemical hydrogen oxidation may be considered a generalization of the results for hydrogen equilibration. Both reactions appear to have a common kinetic step, that of hydrogen dissociative chemisorption. Both reactions appear to be *facile* reactions for the experimental conditions employed. The *facile* nature of these reactions would appear to be due to the properties of the hydrogen dissociation reaction on transition metal surfaces, and it appears that this reaction itself possesses the intrinsic properties of a *facile* reaction.

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