JOURNAL OF CATALYSIS **130**, 268–282 (1991)

Mechanistic Studies of the Isotopic-Exchange Reaction between Gaseous Hydrogen and Palladium Hydride Powder[1]

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Received September 19, 1990; revised February 8, 1991

A detailed mechanism for the isotopic-exchange reaction between gaseous hydrogen and solid palladium hydride is developed which extends previous models for this reaction by specifically including surface reactions. The modeling indicates that there are two surface-related processes that contribute to the overall rate of exchange: the desorption of hydrogen from the surface and the exchange between surface hydrogen and bulk hydrogen. This conclusion is based upon measurements in a flow reactor in which Raman spectroscopy was used to analyze the output of the reactor. This data was used to develop a computer model for the exchange process. In addition, measurements examining the effect of small concentrations of carbon monoxide were helpful in elucidating the mechanism. Carbon monoxide reversibly inhibits certain steps in the exchange; this slows the overall rate of exchange and changes the distribution of products from the reactor.

INTRODUCTION

Heterophase hydrogen isotope exchange in palladium is a fundamental gas–solid interaction that involves the effects of sorption of the gas into the bulk of the solid. The hydrogen/palladium hydride system is of considerable importance in that palladium is widely used as a hydrogenation/dehydrogenation catalyst and the presence of hydrogen in the metal can significantly affect the catalytic properties of the solid (*1*). In other technological applications, palladium is often employed in systems for hydrogen isotope separation and hydrogen purification.

Overall, isotope exchange between gaseous hydrogen and palladium hydride occurs between a gas and a solid. However, between these two phases lies the surface of the solid through which the reactants must pass. This surface and the reactions occurring on it, therefore, have the potential for limiting the rate of the overall exchange reaction. In this paper, a mechanism for the exchange is developed which explicitly considers the role of the surface. This mechanism is based upon measurements of the hydrogen–deuterium exchange in a flow reactor which has been used in previous studies of this system (*2*). In addition, the results of new measurements, in the same reactor, are presented in which the effect of the *gas phase impurities,* carbon monoxide and methane, on the exchange process was examined. These were chosen for study because they may well be present in various catalytic processes. Carbon monoxide, in particular, is found to have a deleterious effect on the exchange. The effect of CO is of interest not only in demonstrating that small concentrations of impurities can poison the exchange reaction, but also in elucidating the mechanism. That is, CO inhibits the exchange reaction by blocking surface sites and therefore reactions involving the surface become more apparent. From these results, an exchange mechanism is developed using computer modeling.

This report is an extension of the previous studies of Foltz and Melius (*2*). In that work, real-time measurements of hydrogen–

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[1] This work is supported by the U.S. Department of Energy under contract number DE-AC0476DP00789.

0021-9517/91 $3.00

deuterium exchange occurring between the solid and gas phases in gaseous hydrogen (deuterium) flows directed through packed-powder beds of palladium deuteride (hydride) were performed. The isotopic composition of the gas (H_2, D_2, HD) exiting from the powder bed was analyzed as a function of time during the exchange process using spontaneous Raman light scattering. The results of those experiments were successfully interpreted in terms of a parametric rate-equation model in which the exchange reaction was modeled using a "single-exchange" mechanism discussed in detail below. The mechanism developed in this paper essentially reduces to the single-exchange mechanism in the absence of impurities. Overall, however, the model presented here yields a more detailed understanding of several aspects of the isotopic-exchange process concerning surface reactions, the importance of the surface area of the powder, and isotope effects.

Many other studies have been performed on the palladium–hydrogen system. Several studies have examined the thermodynamic and equilibrium aspects of the isotope effects in the hydrogen–palladium system and are reviewed by Foltz and Melius (*2*).

EXPERIMENTAL CONDITIONS AND METHOD

The reactor and experimental technique have been described in detail before (*2*) and are only summarized here. A well-characterized open gas-flow reactor was used containing a 1-cm diameter by 20.3-cm long powder bed section. Quasi-spherical, 106- to 124-μm diameter pure palladium powder (D. F. Goldsmith Chemical & Metal Corp., Lot 811-2,3) was packed into the bed section at a packing density of $\sim$7.5 g cm^{-3} (unhydrided porosity $\sim$0.38). The same powder used and characterized in the earlier experiments (*2*) was reused in the present studies. As in the earlier work, the flow channel was evacuated prior to each exchange experiment and the powder bed baked out under high vacuum to a temperature around 475–500 K.

A pressure gauge at each end of the bed section allowed absolute input and output gas pressure measurements to be made and a calibrated mass flow meter provided the volumetric gas-flow rate through the bed. These measurements were made as a function of time during each experiment. Automatic control valves (MKS Instruments, Model 248A/250B) added to the input and output gas lines and slaved to the appropriate pressure gauge were used to maintain desired input and output pressures. With the input and output pressures held constant, the gas-flow rate is determined by the overall conductance of the flow channel and powder bed.

In a typical "clean" exchange experiment in which gas phase impurities *were not* introduced, the palladium powder was deuterided (hydrided) to a known stoichiometry at the desired overpressure. Subsequently, the other isotope, hydrogen (deuterium), was introduced through a fast-acting butterfly valve into the bed section. The absolute partial pressure of D_2 and H_2 in the gas exiting from the bed as a result of the exchange process was measured as a function of time using spontaneous Raman light scattering. While HD can also be detected this way, the concentration cannot be easily calibrated. Therefore, the HD concentration was inferred from the difference between the total output pressure and the H_2 and D_2 partial pressures.

To study the effect of impurities on the exchange process, known concentrations of impurities were seeded into the input gas flow. In these experiments, a clean palladium deuteride bed was prepared as before, but then hydrogen plus contaminant gas flowed into the bed. The impurity-seeded hydrogen gas was obtained by volume mixing techniques in a stainless-steel vessel of known volume instrumented with an absolute pressure gauge (Wallace & Tiernan, Series 1500). High-purity gases were used "as-received" from the vendor (99.9995% pure H_2, 99.99% minimum pure D_2, and 104 ppm CO in H_2 from Air Products & Chemicals;

99.99% pure CO, and 99.992% pure CH_4 from Airco). All impurity gas concentrations in hydrogen are given as parts per million (ppm) or percentage by volume.

It is emphasized that the reactor geometry, particle size and shape, and operating method were deliberately chosen to minimize the effects of gas-flow dynamics in the bed during an experiment in order to examine in detail the surface processes. For the experiments discussed in this report, the input gas pressures used were in the range 1050 to 1200 Torr while the output gas was either at or slightly above atmospheric pressure. The resultant gas-flow rate through the bed was in the range of 0.6 to 1.1 standard liters per minute (slm). All measurements were performed at room temperature.

The error bars given on several of the partial pressure data points (see next section) give the random uncertainty (±2 standard deviations) in the partial pressure determinations and result from a combination of counting statistics errors in the Raman signal (i.e., shot noise), electronics errors, and uncertainties in the total output gas pressure measurement. The (vendor-specified) uncertainties in the measurement of input and output pressures are ±2 Torr and ±1 Torr, respectively. The uncertainty in the measured gas-flow rate results from the calibration of the mass flow meter against the wet test meter and is ±0.02 slm. While a single value for the gas-flow rate has been quoted for each experiment, it should be noted that the flow rate actually monotonically varies somewhat over the course of the experiment due to the changing composition and therefore viscosity of the gas flowing through the bed. The values of the gas-flow rate given are averaged over the duration of each experiment. The extent of the flow variation ranges from ~0.1 slm for clean exchange experiments (significant change in gas composition) to close to the uncertainty limit of the flow measurement (0.02 slm) for highly poisoned exchange experiments (little change in gas composition).

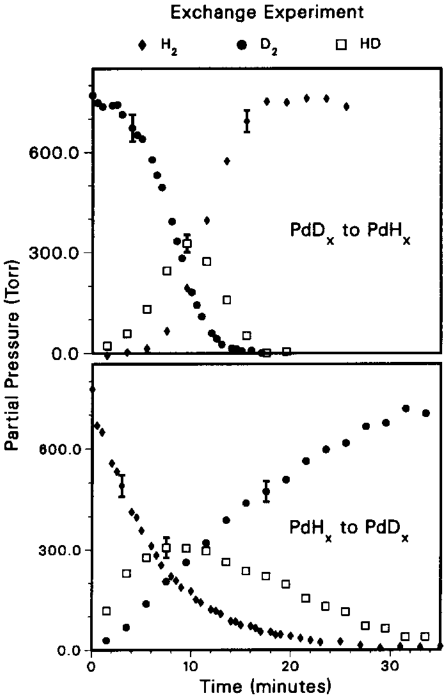

FIG. 1. The gas composition at the outlet of the reactor during clean exchange processes (adapted from Ref. (*2*)).

EXPERIMENTAL RESULTS

Clean Hydrogen and Deuterium Exchange

The results of exchange of palladium deuteride with clean hydrogen and vice versa have been described before (*2*) and so are only summarized here. The composition of the gas at the outlet of the reactor is presented in Fig. 1 as a function of time. At the top of Fig. 1, the conversion of palladium deuteride to palladium hydride (referred to as D-to-H exchange in Ref. (*2*)) is shown. The bottom of Fig. 1 shows the reverse exchange beginning with palladium hydride (H-to-D exchange in Ref. (*2*)).

Two important points are apparent from these clean exchange results. First, the conversion of palladium deuteride to palladium hydride is faster than the reverse reaction. This parallels the exothermicity of the hydride to deuteride conversion whereas the reverse exchange is endothermic. Second,

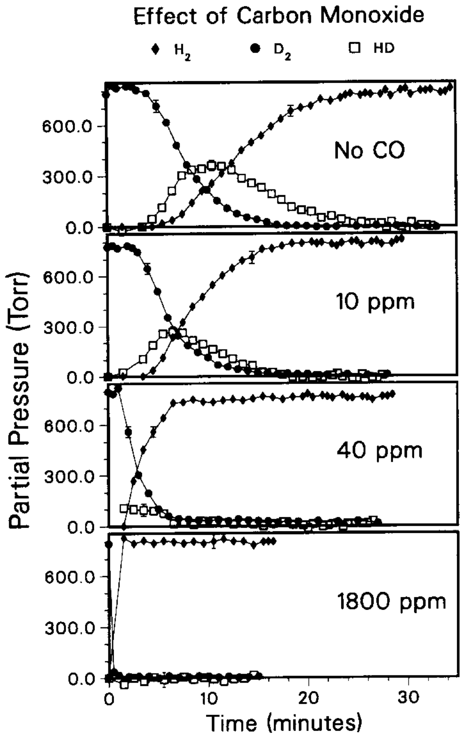

FIG. 2. Experimental results showing that carbon monoxide introduced into the input hydrogen gas flow inhibits the exchange reaction. The lines connecting the data points are only to aid the eye.

the gases are nearly in isotopic equilibrium at the outlet of the reactor. That is, the amount of HD is nearly as large as that expected for an equilibrium mixture of H_2, HD, and D_2. This is most apparent at the time where the H_2 and D_2 curves cross at which point the HD concentration is nearly twice that of H_2 or D_2.

Effects of Impurity Gases

The effect of various concentrations of carbon monoxide on the composition of the gas at the reactor outlet is presented in Fig. 2. In the poisoning experiments, only the conversion of palladium deuteride to palladium hydride was examined. At the top of Fig. 2, the results for a clean exchange are shown for reference. In the rest of the figure results are shown for increasing levels of CO impurity: approximately 10, 40, and 1800 ppm of CO in hydrogen, respectively. For these experiments, the input and output pressures were 1206 and 801 Torr, respectively; gas-flow rates of 0.81, 0.80, 0.74, and 1.05 slm were measured for the clean, 10, 40, and 1800 ppm CO experiments, respectively.

Several effects are evident, the most obvious of which is that with increasing CO concentration, the bed is deactivated at shorter periods of time. That is, the time for the gas reactant (in this case H_2) to appear unexchanged at the outlet, is reduced with increasing CO concentration. Poisoning by CO is apparent at concentrations as low as 10 ppm and isotopic exchange is completely inhibited at 1800 ppm. The amount of deuterium which can be exchanged from the bed, as determined from the total amount of D_2 and HD flowing out of the reactor, decreases with increasing amounts of CO. For the results shown in Fig. 2, at the approximate CO concentrations of 10, 40, and 1800 ppm, the amount of deuterium which was exchanged from the powder was 95, 40, and 0%, respectively.

CO inhibits the exchange by blocking surface sites. Referring to the results in Fig. 2, when the amount of CO flowing into the bed is approximately equal to a monolayer (determined from flow rate and CO concentration level), the exchange was inhibited. This indicates that CO inhibits the reaction by blocking surface sites. Experiments also indicate that this effect was reversible. That is, when the CO impurity was removed from the input gas and pure hydrogen flowed through the reactor, the exchange activity of the bed was restored.

Another important effect due to the presence of CO is apparent from the data shown in Fig. 2 and provides insight into the mechanism of the exchange reaction. The H_2, HD, and D_2 concentrations flowing out of the reactor are not in isotopic equilibrium when CO is present. In particular, the HD concentration is significantly below that at equilibrium. This means that the single-exchange mechanism (requiring isotopic equilibrium)

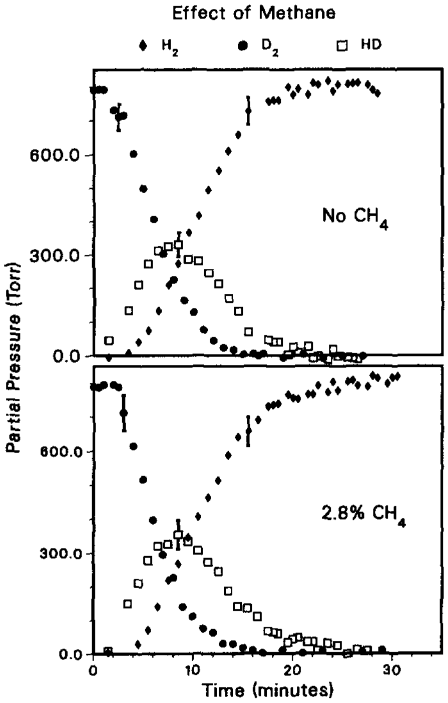

FIG. 3. Experimental results showing that methane does not inhibit the exchange reaction at concentrations up to 2.8% in the input hydrogen gas flow.

which was previously used to model the clean exchange reaction with reasonable success is no longer valid when poisons are present as discussed in detail below.

The effect of methane on the exchange process is shown in Fig. 3. Again, the results for a clean exchange are shown for comparison. For the clean experiment, the input and output pressures were 1204 and 800 Torr, respectively, and the gas-flow rate was 1.03 slm. For the methane-seeded experiment, the input and output pressures and flow rate were 1211 Torr, 806 Torr, and 1.04 slm, respectively. The isotopic concentrations at the output of the reactor with 2.8% CH_4 in the input hydrogen gas are essentially identical to the clean experiment and so it is concluded that methane does not adversely affect the exchange reaction. This is not surprising because methane bonds only weakly to most surfaces.

REACTION MECHANISM

Previous Models

A detailed model for the exchange is potentially quite complicated because many elementary reaction steps occur including: adsorption, desorption, dissociation, recombination, surface diffusion, bulk diffusion, surface-bulk exchange, and gas phase transport. Typical experiments with a powder and a flowing gas are not detailed enough to determine all aspects of such a process because of the complexity of the system. Under many conditions, however, only a few steps are rate-determining so that a much simpler mechanism can be used in modeling the reaction. A simple approach for such situations is to conceptually divide the system into two phases, gas and solid, and lump together all of the interface reactions into an *overall* reaction. In the past, two such mechanisms have been considered for this heterophase-exchange reaction.

The first and most successful kinetic model employs the *single-exchange* mechanism which consists of the following set of reactions:

$$H_2\,(g) + D\,(b) \rightleftarrows HD\,(g) + H\,(b) \quad (1)$$

$$HD\,(g) + D\,(b) \rightleftarrows D_2\,(g) + H\,(b), \quad (2)$$

where (g) and (b) refer to components in the gas and solid phases, respectively. In this mechanism, a molecule of hydrogen can only exchange one atom in each encounter with the solid. For example, H_2 can exchange one atom with the solid to form HD but cannot exchange two atoms to form D_2 during one encounter with the solid. This single-exchange mechanism was used by Foltz and Melius (*2*) in their model of the isotope exchange reaction. The predictions of the single-exchange mechanism are shown in Fig. 4 in comparison with the experimental measurements.

An important consequence of this mechanism is that the H_2, HD, and D_2 concentrations at the outlet of the reactor are in isotopic equilibrium. This consequence is not immediately obvious from the mechanism

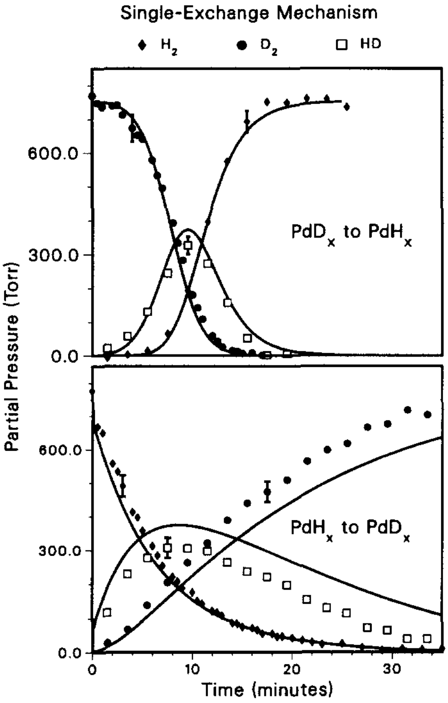

FIG. 4. Comparison of the predictions of the single-exchange model to the experimental results (adapted from Ref. (*2*)).

but is intuitively reasonable. For example, in the mechanism shown above, the only route from H_2 to D_2 is through HD, which suggests that the concentration of HD cannot stray far from equilibrium. This model fits the experimental data partly because the measured gas concentrations are, indeed, near equilibrium as shown in Fig. 1. The mechanism is inadequate, however, to account for the exchange in the presence of a carbon monoxide impurity where the gases are not in isotopic equilibrium as shown in Fig. 2.

An alternative overall reaction which has been considered is the *multiple-exchange* mechanism which consists of the following set of reactions:

$$H_2\,(g) + D\,(b) + D\,(b) \rightleftarrows D_2\,(g) + H\,(b) + H\,(b) \quad (3)$$

$$H_2\,(g) + H\,(b) + D\,(b) \rightleftarrows HD\,(g) + H\,(b) + H\,(b) \quad (4)$$

$$HD\,(g) + D\,(b) + D\,(b) \rightleftarrows D_2\,(g) + H\,(b) + D\,(b). \quad (5)$$

In this mechanism, a molecule of hydrogen can exchange one or both atoms in each encounter with the solid. For example, H_2 can exchange one atom with the solid to form HD or can exchange two atoms to form D_2 during a single encounter with the solid. In contrast to the single-exchange mechanism, the multiple-exchange mechanism does not require that H_2, HD, and D_2 be in isotopic equilibrium. Intuitively, the reason for this is that D_2 can be formed directly from H_2 in a single encounter with the surface without forming HD as an intermediate. The modeling studies presented in Ref. (*2*) indicated that the multiple-exchange mechanism provided a poor description of the H/D/Pd exchange process under clean conditions in that it severely underestimated the HD concentration in the output gas flow.

Surface-Exchange Model

The problem with the single- and multiple-exchange mechanisms is that they are phenomenological in nature and do not *explicitly* consider the role of the surface in the exchange. The CO experiments, however, indicate that the surface is important.

A more general and microscopic mechanism is developed here called the *surface-exchange* model which specifically considers the role of the surface in the exchange. This is accomplished by dividing the overall exchange process into three phases (gas, bulk, and surface), and examining the transport of hydrogen between them and how CO affects that transport. Figure 5 is a schematic diagram of the proposed mechanism. There are two reactions which link the gas and the surface: adsorption (step 1) and desorption (step 3), and one reaction which links the surface with the bulk (step 2). In addition, CO can non-dissociatively and reversibly adsorb on the surface of the palladium hydride:

$$CO\,(g) \rightleftarrows CO\,(a). \quad (6)$$

The mechanism shown in Fig. 5 is based

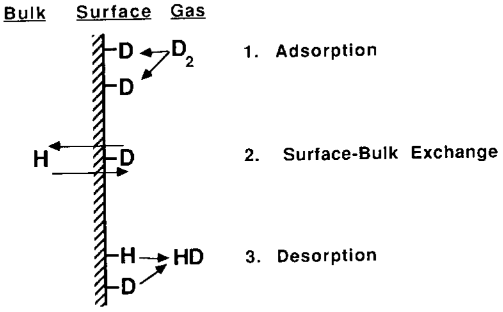

FIG. 5. The three reaction steps included in the surface-exchange mechanism.

upon the typical chemistry observed for hydrogen on surfaces. Hydrogen is best understood on metal surfaces, where, in general, the reactions proceed via dissociation (*3*). For example, the absorption of hydrogen into bulk palladium proceeds via chemisorbed hydrogen under normal conditions (*4, 5*). Dissociative adsorption of hydrogen (step 1) and recombinative desorption (step 3) are, therefore, reasonable steps to include in the model for the isotopic-exchange reaction on palladium hydride. In this model, steps 1 and 3 are considered to be elementary reactions.

The second step in the proposed mechanism is less well understood from a fundamental standpoint; however, experiments with hydrogen absorption into *metallic* palladium suggest that this step is important in the exchange. For example, in the case of metallic palladium, hydrogen bonds more strongly to the surface than to the bulk, so that there is an energy barrier between hydrogen on the surface and in the bulk (*5, 6*). Step 2 is not actually an elementary reaction since the movement of surface hydrogen to the bulk and vice versa are probably separate elementary reactions just as adsorption and desorption are separate steps. The lack of information about these processes, however, does not allow the steps to be resolved and so they are combined in the mechanism into one overall step.

A mathematical formulation of the mechanism shown in Fig. 5 will be presented later, but first intuitive arguments are presented to show that it accounts for the general features of the exchange reaction. First, consider the exchange in the absence of CO and assume that the overall exchange is controlled by surface-bulk exchange (step 2). That is, the rates of adsorption and desorption of hydrogen (steps 1 and 3) are fast compared to the rate of surface-bulk exchange. The mechanism is now consistent with several aspects of the H/D/Pd exchange. First, it is observed that the gases at the outlet of the reactor are near isotopic equilibrium under clean conditions. The assumption of fast adsorption and desorption would result in equilibrium, because the facile adsorption and desorption steps allow the hydrogen and deuterium atoms to mix on the surface and, therefore, drive the gas phase composition to equilibrium. Second, this mechanism essentially reduces to the single-exchange mechanism in the absence of CO. That is, assuming the adsorption and desorption processes are faster than the surface-bulk exchange implies that the residence time for a molecule on the surface is shorter than the period for surface-bulk exchange. A molecule, therefore, will be resident on the surface long enough to exchange, at most, one atom before desorbing, which is equivalent to the reactions allowed in the single-exchange mechanism Eqs. (1) and (2).

Consider now the effect of CO on the mechanism shown in Fig. 5. Assume that CO is bonded to the surface more strongly than hydrogen so that it has a longer residence time on the surface. This will directly inhibit the adsorption of hydrogen (step 1) because there are fewer free sites on the surface. CO affects surface-bulk exchange and desorption (steps 2 and 3) by reducing the concentration of hydrogen and deuterium atoms on the surface. Intuitively, this will have several effects on the overall exchange reaction. First, because step 1 is a necessary step in the overall exchange, CO, by inhibiting that step, will slow and then eventually stop the exchange process altogether. Second, in the presence of CO, non-equilibrium concentrations of HD appear at the reactor outlet. In the unpoisoned reaction it was assumed that facile adsorption and desorption allowed the mixing of the hydrogen and deuterium atoms which resulted in equilibrium. If CO blocks the adsorption step, however, the pathway to equilibrium is inhibited, and the gas phase will no longer be in equilibrium. Third, the concentrations of HD produced in the presence of CO will be reduced *below* equilibrium levels. The reduced concentration of surface hydrogen will reduce the rate of desorption which will result in longer residence times on the surface for hydrogen. At residence times which are long compared to the period for surface-bulk exchange, the molecules will exchange both atoms while on the surface. Therefore, more homonuclear molecular hydrogen will be produced at the expense of heteronuclear HD. All of these features are consistent with the behavior of the exchange in the presence of CO.

The modeling will largely substantiate this intuitive version of the model. The modeling indicates, however, that the adsorption and desorption reactions do not need to be overwhelmingly fast to account for isotopic equilibrium. Indeed, because the gas concentrations at the outlet of the reactor under clean conditions are actually observed to deviate somewhat from isotopic equilibrium, the model indicates that the rates of desorption and of surface-bulk exchange are comparable.

MATHEMATICAL MODEL

Although the mechanism shown in Fig. 5 appears intuitively correct, a mathematical formulation of the model is needed to verify the mechanism. The model discussed here is an adaptation of the model developed by Foltz and Melius (*2*) and incorporates the mechanism illustrated in Fig. 5. A computer code was written to test the model so that the measured output of the reactor could be compared with that predicted by the model. In the computer model, the reactor is treated as a one-dimensional tube which is conceptually divided into a series of 100 zones. The concentrations of the various species are assumed to be uniform within each zone and these concentrations used to predict the rate of the reactions shown in Fig. 5. The flow rate of the gas through the reactor is calculated from the gradient of the gas pressure between adjacent zones using Darcy's law. A stiff differential equation solver is required to solve the equations. Approximately 3 min of real time (i.e., wall clock time) is required on a CRAY Y-MP to run the model for the unpoisoned exchange. The carbon monoxide impurity, however, makes the problem "stiffer" so that longer computations times are needed. For example, approximately 90 min were required to run the model for the case of 100-ppm CO impurity.

Because the role of the surface is specifically considered in the exchange mechanism and because the gas phase species need not be in isotopic equilibrium, account must be kept of a variety of species including: H_2 (*g*), HD (*g*), D_2 (*g*), H (*a*), D (*a*), H (*b*), and D (*b*), plus, in the case of the CO-poisoned experiments, CO (*g*) and CO (*a*). Here (*g*), (*a*), and (*b*) refer to species in the gas, surface, and bulk phases, respectively. The concentrations of these species are denoted with square brackets around the chemical symbol and are specified in units of molecule cm^{-3} for gas and bulk species and molecule cm^{-2} for surface species.

The concentrations of the various species are affected by four processes: the three reactions shown in Fig. 5 and the transport of gas through the reactor. Table 1 summarizes the differential equations that are used to describe how the various species concentrations are affected by the four processes. For example, the equations for the gas phase in Table 1 show that the change in the concentration of H_2 with respect to time, $\partial[H_2]/\partial t$ (with units of molecule cm^{-3} s^{-1}), de-

TABLE 1

Differential Equations Used in the Surface-Exchange Model

Flow	Adsorption	Desorption	Exchange
	Gas		
$\frac{\partial[H_2]}{\partial t} = \frac{-\partial([H_2]V_f)}{\partial x} + \frac{S_0(1-\phi)}{\phi} \times$	$(\ -R^{ads}_{H_2}$	$+R^{des}_{H_2} \ )$	
$\frac{\partial[HD]}{\partial t} = \frac{-\partial([HD]V_f)}{\partial x} + \frac{S_0(1-\phi)}{\phi} \times$	$(\ -R^{ads}_{HD}$	$+R^{des}_{HD} \ )$	
$\frac{\partial[D_2]}{\partial t} = \frac{-\partial([D_2]V_f)}{\partial x} + \frac{S_0(1-\phi)}{\phi} \times$	$(\ -R^{ads}_{D_2}$	$+R^{des}_{D_2} \ )$	
$\frac{\partial[CO]}{\partial t} = \frac{-\partial([CO]V_f)}{\partial x} + \frac{S_0(1-\phi)}{\phi} \times$	$(\ -R^{ads}_{CO}$	$+R^{des}_{CO} \ )$	
	Surface		
$\frac{\partial[H]}{\partial t} =$	$2R^{ads}_{H_2} + R^{ads}_{HD}$	$-2R^{des}_{H_2} - R^{des}_{HD}$	$+R^{exch}$
$\frac{\partial[D]}{\partial t} =$	$2R^{ads}_{D_2} + R^{ads}_{HD}$	$-2R^{des}_{D_2} - R^{des}_{HD}$	$-R^{exch}$
$\frac{\partial[CO]}{\partial t} =$	R^{ads}_{CO}	$-R^{des}_{CO}$	
	Bulk		
$\frac{\partial[H]}{\partial t} =$			$-S_0R^{exch}$
$\frac{\partial[D]}{\partial t} =$			$+S_0R^{exch}$

pends upon three of the four processes. The first term,

$$\frac{-\partial([H_2]V_f)}{\partial x},$$

accounts for the one-dimensional flow of the gas through the bed which depends upon the concentration of H_2 (*g*) as a function of the axial position, *x*, along the bed, and upon the velocity of gas, V_f. In the second term, $-R^{ads}_{H_2}$ (with units of molecule cm^{-2} s^{-1}) is the rate of adsorption of H_2 (*g*) (step 1 in Fig. 5). In the third term, $+R^{des}_{H_2}$ (with units of molecule cm^{-2} s^{-1}) is the rate of desorption of H_2 (*g*) (step 3 in Fig. 5). The rates of adsorption and desorption are multiplied by S_0 $(1 - \phi)/\phi$ to convert from the rate for a surface process (with units of molecule cm^{-2} s^{-1}) to the rate for the overall exchange (with units of molecule cm^{-3} s^{-1}). That is, the gas phase rates, R_{gas}, are related to surface rates, $R_{surface}$, by

$$R_{gas} = R_{surface} \frac{S}{V_{gas}},$$

where S is the total surface area and V_{gas} is the volume of the gas. From this it follows that

$$\begin{aligned} R_{gas} &= R_{surface} S_0 \frac{V_{solid}}{V_{gas}} \\ &= R_{surface} S_0 \frac{V_{total} - V_{gas}}{V_{gas}} \end{aligned}$$

$$= R_{\text{surface}}\, S_0 \left(\frac{1}{\phi} - 1\right)$$

$$= R_{\text{surface}}\, S_0 \left(\frac{1-\phi}{\phi}\right),$$

where S_0 is the specific surface of the powder (powder surface area per unit solid volume), ϕ is the porosity of the bed (void volume divided by the reactor volume), and V_{total} is the sum of the gas and solid volume.

The concentrations of the surface species are not directly affected by gas phase flow but are affected by adsorption, desorption, and surface-bulk exchange. For example, the time-rate-of-change of the adsorbed hydrogen concentration, $\partial[\mathrm{H}]/\partial t$ consists of $2R^{\text{ads}}_{\mathrm{H_2}} + R^{\text{ads}}_{\mathrm{HD}}$ (adsorption of H_2 and HD); $-2R^{\text{des}}_{\mathrm{H_2}} - R^{\text{des}}_{\mathrm{HD}}$ (desorption of H_2 and HD); and R^{exch} (surface-bulk exchange).

The concentrations of the H (*b*) and D (*b*) depend only upon the rate of surface-bulk exchange, $S_0 \times R^{\text{exch}}$. R^{exch} is multiplied by S_0 to convert from the rate for a surface process (with units of atoms $\mathrm{cm^{-2}\ s^{-1}}$) to the rate for a bulk process (with units of atoms $\mathrm{cm^{-3}\ s^{-1}}$).

Next, detailed equations for the rates of adsorption, desorption, and surface-bulk exchange are presented which depend upon the local concentrations of the various species. The rate of *adsorption* for all of the gaseous species has the same form:

$$R^{\text{ads}}_X = (\text{flux}\, X) \times (\text{fraction of free area on surface}) = \frac{P_X N_a}{(2\pi R_0 M T)^{1/2}} \left(1 - \sum_i^{\text{all adsorbates}} \frac{[X_i(a)]}{[X_i(a)]_{\max}}\right), \tag{7}$$

where the R^{ads}_X is the rate of adsorption (with units of molecule $\mathrm{cm^{-2}\ s^{-1}}$) of X ($X = \mathrm{H_2}$, HD, D_2, and CO); P_X is the partial pressure of X; N_a is Avogadro's constant; R_0 is the universal gas law constant, M is the (molar) molecular weight of X; T is the absolute temperature; $[X_i\ (a)]$ is the concentration of adsorbed species *i*; and $[X_i\ (a)]_{\max}$ is the maximum concentration of adsorbed species *i*. The expression for the flux of molecules striking the surface is taken from the kinetic theory of gases which is described, for example, in Dushman (*7*). Often a sticking coefficient is included in this equation, but in this case it is assumed to be unity.

The rate of *desorption* of the hydrogen- and deuterium-containing species is second order:

$$R^{\text{des}}_{\mathrm{H_2}} = k^{\text{des}}_{\mathrm{H_2}} [\mathrm{H}\,(a)]^2 \tag{8a}$$

$$R^{\text{des}}_{\mathrm{HD}} = 2k^{\text{des}}_{\mathrm{HD}} [\mathrm{H}\,(a)][\mathrm{D}\,(a)] \tag{8b}$$

$$R^{\text{des}}_{\mathrm{D_2}} = k^{\text{des}}_{\mathrm{D_2}} [\mathrm{D}\,(a)]^2, \tag{8c}$$

while the desorption of CO is first order:

$$R^{\text{des}}_{\mathrm{CO}} = k^{\text{des}}_{\mathrm{CO}} [\mathrm{CO}\,(a)], \tag{9}$$

where R^{des}_X is the rate (with units of molecule $\mathrm{cm^{-2}\ s^{-1}}$) and k^{des}_X is the rate constant for desorption of X ($X = \mathrm{H_2}$, HD, D_2, and CO).

The rate of *surface-bulk* exchange is defined for the reaction

$$\mathrm{D}\,(a) + \mathrm{H}\,(b) \rightleftarrows \mathrm{D}\,(b) + \mathrm{H}\,(a) \tag{10}$$

and has the net rate expression

$$R^{\text{exch}} = \frac{k^{\text{exch}}}{[\mathrm{H}\,(b)]_{\max}} \left(\frac{1}{\sqrt{\alpha}} [\mathrm{D}\,(a)][\mathrm{H}\,(b)] - \sqrt{\alpha}\, [\mathrm{H}\,(a)][\mathrm{D}\,(b)]\right), \tag{11}$$

where R^{exch} is the rate (with units of atoms $\mathrm{cm^{-2}\ s^{-1}}$) and k^{exch} the rate constant for surface-bulk exchange. The surface-bulk exchange is not an elementary reaction; rather it is similar to the equation used to model the single-exchange mechanism. A gas-to-solid-phase isotope effect is specifically included in this reaction in terms of the parameter α, the isotope separation factor, analogous to the previous modeling of the single-exchange mechanism (*2*).

Although this mechanism is significantly more complex than the single- or multiple-

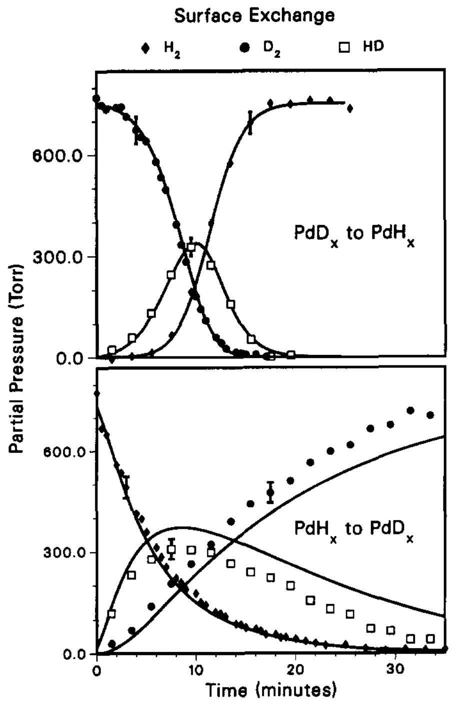

FIG. 6. Comparison of the predictions of the surface-exchange model to the experimental results for the exchange in the absence of impurities.

exchange mechanisms used previously, several simplifying assumptions are used. These assumptions are needed because of the present lack of more detailed information and to keep the problem tractable. Among the assumptions which are implicit in this model are that the desorption rates do not depend upon coverage; that hydrogen, deuterium, and carbon monoxide do not interact on the surface; and that all of the hydrogen isotope effects which are present in the interface processes are combined in the surface-bulk exchange step.

MODELING RESULTS

The results of the surface-exchange model are shown in Figs. 6 and 7. In order to be acceptable, the new mechanism should model the *unpoisoned* exchange at least as well as the single-exchange mechanism, and Fig. 6 shows that this is indeed the case. There is marginal improvement in the HD concentration model results using the surface-exchange mechanism. The single-exchange model assumes isotopic equilibrium and so overestimates the amount of HD produced by the exchange (Fig. 4). The surface-exchange model (Fig. 6), in contrast, is able to predict more accurately the HD production.

Currently, the surface-exchange model does not improve significantly upon the fit for the hydride-to-deuteride exchange, in comparison to the single-exchange mechanism. There are several possible explanations for the discrepancy between the experiment and the model, but a major concern is the primitive level at which the isotope

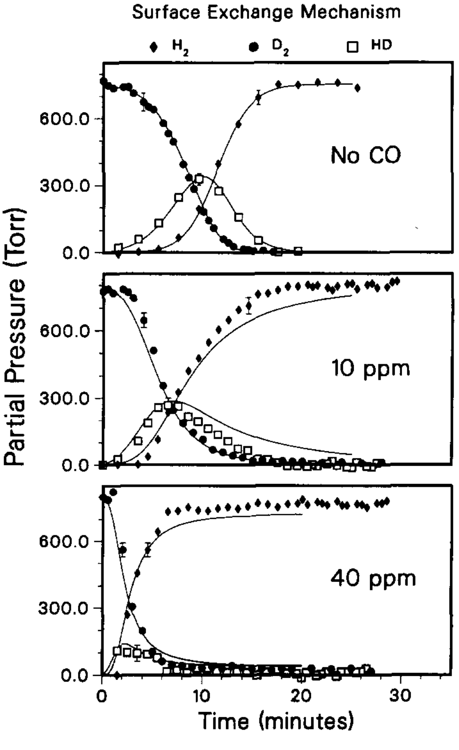

FIG. 7. Comparison of the predictions of the single-exchange model to the experimental results for the exchange in the presence of carbon monoxide.

effects have been included so far in the modeling. That is, the isotope effects have been ignored in the adsorption and desorption reactions. The model could accommodate isotope effects in these reactions by using different values for k_X^{des} for each species X ($X = H_2$, HD, and D_2) in the desorption rate expressions Eqs. (8a)–(8c), but experimental values are not available regarding the relative values of these quantities, and there would be too many parameters to be meaningfully derived from the experimental data. Therefore, the isotope effects have been lumped together in the surface-bulk exchange step. This assumption is less correct, however, for the hydride-to-deuteride conversion, because the larger mass of D_2 results in a lower impingement rate Eq. (7). This enhances the importance of the adsorption and desorption reactions relative to the surface-bulk exchange in the overall kinetics and in the isotope effects. Thus, ignoring the isotope effects in desorption results in a poorer fit for the hydride-to-deuteride conversion. There may also be other effects which are currently not included in this model such as localized heating (or cooling) in the exchange zone due to the exothermicity (or endothermicity) of the exchange reaction, and varying degrees of channeling in the bed due to the difference in volume expansion between palladium hydride and palladium deuteride. See Ref. (*2*) for a discussion of these effects.

Figure 7 shows that the surface-exchange model predicts well many aspects of the exchange which is *poisoned* by carbon monoxide. First, the model mimics the effects of increasing CO concentration including the poisoning of the bed and the appearance of H_2 at the outlet of the reactor at increasingly shorter time periods. Second, the model predicts that the HD concentration should fall considerably below isotopic equilibrium as observed. The model also can account for the reversible poisoning by CO because it allows CO to desorb by the reverse of the reaction in Eq. (6).

KINETIC PARAMETERS

The validity of the model depends not only upon the comparison to experiment but also upon the reasonableness of the kinetic parameters used in the model. In this section the values of the important kinetic parameters in Eqs. (7)–(9), (11) are considered. Ideally, the kinetic parameters are derived directly from an experimental measurement, but some of the parameters cannot be measured and are therefore obtained by fitting the model results to the experimental data. Most of the parameter values used appear to be reasonable in comparison to other systems.

In Eq. (7), the important parameters are $[X_i\,(a)]_{\text{max}}$, the maximum coverages of the various adsorbates. The maximum coverages of both hydrogen and deuterium used in the modeling is 1×10^{15} atoms cm^{-2}. This value is quite close to the saturation coverage of 9.4×10^{14} atoms cm^{-2} for hydrogen on a Pd(110) surface (*8*). The maximum coverage of carbon monoxide used in the modeling was 3.9×10^{14} molecule cm^{-2}. This value was obtained by fitting to the data, but is reasonable by comparison to carbon monoxide adsorption on a Pd(111) surface where, although the behavior is complex, the maximum CO coverage is in the range of $3–5 \times 10^{14}$ molecule cm^{-2} (*9*).

In Eqs. (8a)–(8c), the important kinetic parameters are the desorption rate constants for H_2, HD, and D_2. These are critical parameters for the model which, unfortunately, are difficult to measure directly. The same value, 4.9×10^{-13} cm^2 s^{-1}, was used for all three of these rate constants in the modeling and was obtained by fitting to the data. The magnitude of this is in the range of 2.8×10^{-11} cm^2 s^{-1} which is estimated from thermal desorption measurements of hydrogen from palladium hydride (*10*). This estimate is obtained by dividing the zero-order rate constant at 300 K of the original work to second-order form by dividing by $[H\,(a)]^2_{\text{max}}$. This is a crude estimate, however, so that precise agreement between the two numbers cannot be expected. Both of these values are substantially larger than the desorption rate constant of 1.5×10^{-18} cm^2 s^{-1} for chemisorbed hydrogen (β state) from Pd(111) at 300 K (*5*). This is not surprising, however, because hydrogen is adsorbed on palladium hydride much less strongly than on palladium metal. As discussed above, the same value of k^{des} was used for H_2, HD, and D_2, because the experimental exchange data was not sufficiently detailed to determine each of these parameters separately. This means that isotope effects in the desorption step are left out of the modeling. Better agreement to experiment would be expected, particularly for the hydride to deuteride conversion, if these were known more precisely.

In Eq. (9), the important kinetic parameter is the desorption rate constant for CO. This parameter is also difficult to measure directly. The value of $k_{\text{CO}}^{\text{des}}$ used in the modeling was 4.0×10^{-4} s^{-1} which was obtained by fitting to the data. There is no measurement of CO desorption from palladium hydride, so the closest comparison is to palladium metal, where the desorption rate constant is 1.0×10^{-10} s^{-1} on the Pd(331) surface at 300 K (*11*). This is, of course, substantially smaller than the value used in the modeling, because carbon monoxide is expected to be adsorbed on palladium hydride much less strongly than on palladium metal.

In Eq. (11), the important kinetic parameters are k^{exch} and α, the rate constant for surface-bulk exchange and the isotope separation factor, respectively. The value of k^{exch} used in the modeling is 2000 s^{-1} and is obtained by fitting to the data. For comparison, a rate constant equivalent to 1207 s^{-1} is used by Foltz and Melius (*2*). This value is obtained by converting their single-exchange rate expression and units to the form of Eq. (11) above. The value used in the modeling here is faster than that of Foltz and Melius because the surface-bulk exchange occurs in series with the adsorption and desorption steps which also contribute to the rate of the overall exchange. The value of α used in the modeling is 2.4 and is the same as that used by Foltz and Melius (*2*).

S_0 was calculated to be 505 cm^{-1} from the average hydrided particle size assuming that the particles are spherically shaped. Micrographs of the powder show that the particles are, in fact, nearly spherical (*2*). The value of the hydrided bed porosity, ϕ, which was used was 0.321.

ASPECTS OF THE MODEL

To the extent that the model is based upon elementary reactions, it can be used to provide a microscopic view of the exchange. For example, a consideration of the pressure at which the exchange was measured (approximately 1 atm) and the rate of desorption of hydrogen, indicates that the surface is almost completely covered with hydrogen under the conditions of the experiment with only about 1 site in 2.5×10^6 being vacant. Thus, 2.5×10^6 collisions with the surface must occur before a molecule is adsorbed. For comparison, this is the same magnitude as the 10^7 collisions which Foltz and Melius estimated that a molecule must experience before exchange occurs (*2*). Of course, the number of collisions required in the present model for *adsorption* is less than the number of collisions required in the single-exchange model for *exchange*, because adsorption is only one step in the exchange process (i.e., an atom can still desorb before undergoing exchange). In the presence of CO, the number of vacant sites decreases even more to less than 1 in 10^8 which is one consequence of the poisoning effect of CO on the exchange.

The model also provides an estimate for the residence times of the various molecules on the surface and the time required to swap a surface atom with the bulk. The residence time is defined as the time required to decrease the concentration by $1/e$. At saturation coverage the residence time for a hydrogen atom on the surface is

$$\begin{aligned}\tau_{\mathrm{H}} &= (k^{\mathrm{des}}_{\mathrm{H}_2} \times [\mathrm{H}\,(a)] + k^{\mathrm{des}}_{\mathrm{HD}} \times [\mathrm{D}\,(a)])^{-1} \\ &= 2.0\,\mathrm{ms}. \qquad (12)\end{aligned}$$

This residence time increases in the presence of CO, however, because [H (*a*)] and [D (*a*)] decrease. In comparison, the residence time for carbon monoxide is much greater

$$\begin{aligned}\tau_{\mathrm{CO}} &= (k^{\mathrm{des}}_{\mathrm{CO}})^{-1} \\ &= 2500\,\mathrm{s}. \qquad (13)\end{aligned}$$

Thus CO stays on the surface much longer than H_2 which accounts for the poisoning of the exchange by CO, but does eventually desorb which is why the poisoning effect is reversible. Finally, the characteristic time for the surface-bulk exchange of a hydrogen atom during a deuteride-to-hydride conversion, for example, is

$$\begin{aligned}\tau_{\mathrm{exch}} &= \left(k^{\mathrm{exch}} \sqrt{\alpha}\, \frac{[\mathrm{D}\,(b)]}{[\mathrm{D}\,(b)]_{\mathrm{max}}}\right)^{-1} \\ &= 0.32\,\mathrm{ms}. \qquad (14)\end{aligned}$$

initially, although this time is inversely related to [D (*b*)] and hence increases. Thus surface-bulk exchange and desorption contribute significantly to the overall rate of the exchange.

One feature of the model which deserves note is the first order dependence of the rate of adsorption of hydrogen and deuterium on the number of surface sites Eq. (7). Intuition, however, might suggest that since the dissociative adsorption of hydrogen or deuterium on a surface requires two surface sites, the adsorption should be second order with respect to the number of surface sites. Early modeling efforts were actually based upon the second-order assumption, but a poor fit to the CO-poisoned experiments was obtained, because it has too strong of a dependence upon the number of surface sites. It was found, for example, with the second-order assumption, that the crossover time of the model could be matched to experiment, but then the model predicted that the overall exchange would be abruptly stopped sooner than observed in the experimental results. Conversely, when the parameters of the model were selected to match the total exchange time in the experiment, then the time for crossover was overestimated. In contrast, with the first-order assumption used in the final version of the model, the crossover times and total exchange time can be reasonably matched to the experiment. The first-order dependence on the number of free sites suggests that hydrogen dissociatively adsorbes via a mobile precursor which can hop around the surface to find two empty sites.

There is another quite different microscopic mechanism for the exchange which was considered and ruled out based on intuitive arguments. This mechanism was considered because of vacuum studies of hydrogen desorption from palladium at low temperatures which suggested that bulk hydrogen in palladium could desorb directly without involving hydrogen adsorbed on the surface of the metal (*12*). To accomplish this, it was proposed that bulk hydrogen exited the solid via defects or special sites on the surface. If this mechanism were applied to the exchange experiments here, however, the exchange would be especially sensitive to poisoning agents such as CO, because only a few sites would need to be poisoned. The experiments with CO, however, show that one monolayer of CO is required to poison the exchange so that the entire surface must be covered to inhibit the exchange. Therefore, it is concluded that the entire surface is involved in the exchange, and that special or defect sites are not required under normal conditions. Special sites may become important at low temperatures, however, where small differences in the energetics at various sites will have a larger effect upon the rate of the exchange. That is, at low temperatures those sites which are energetically favorable for exchange may dominate the exchange process.

Finally, several shortcomings of the current model should be mentioned that future experiments may be able to resolve. The first problem is the lack of information about the isotope dependence of the various reactions. This problem has been discussed in detail above including its effect on the results. A second problem which has not been mentioned is the lack of information at various temperatures. All of the work of the present study was performed at 300 K so no information about activation energies is obtained. A final assumption which limits the present work is that the stoichiometry of the bed does not change.

SUMMARY

The surface processes occurring during the isotopic exchange between gaseous hydrogen and palladium hydride powder have been investigated with measurements in an exchange reactor and modeling of the results.

A more detailed mechanism for the exchange is developed which indicates that two surface-related processes contribute to the overall rate of exchange: desorption and surface-bulk exchange. This more detailed mechanism is required to understand nonequilibrium amounts of HD which can be produced in an exchange reactor and the effects of poisons such as CO which inhibit the exchange by blocking surface sites. Under normal conditions, however, the exchange kinetics can be largely described by a relatively simple, single-exchange mechanism, which has been previously employed (*2*) in which one atom of a gas phase molecule exchanges with the solid at a time.

Carbon monoxide strongly inhibits the exchange by blocking surface sites. The amount of CO required to inhibit the exchange indicates that the exchange process does not require special sites on the surface; instead the entire surface is active. The effect of CO on the exchange is apparent at sustained concentrations of 10 ppm or more.

ACKNOWLEDGMENTS

The authors acknowledge useful discussions with D. Cowgill, S. Griffiths, B. Kay, C. Melius, and R. Stulen. The technical assistance of F. H. Blair and D. Dominguez in conducting the experiments is gratefully acknowledged.

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