

Studies of the Surface and Catalytic Properties of Boron Phosphate with Isotopic Molecules

I. The Interaction of D₂

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When gas phase deuterium is contacted with boron phosphate at elevated temperatures, HD and H₂ are produced in the gas phase in proportions of approximately 2:1, respectively. The existence of exchangeable hydrogen atoms on the surface in quantities up to 1.3×10^{-6} mole/m² is demonstrated, and empty sites, apparently not previously occupied by hydrogen atoms, can be shown to exist in concentrations as high as 1.5×10^{-6} mole/m².

INTRODUCTION

The utility of studies of the reactions of isotopic species with solids for the determination of its surface and catalytic properties is now well known (1, 2). As a result of its availability and relative ease of measurement, and the presence of hydrogen bound to the surface of many catalytic solids, deuterium has for a number of years been used as a probe for surfaces.

One of the first applications of deuterium for surface studies was by Lee and Weller (3) who used deuterium exchange with the surface as a means of measuring the concentrations of surface hydroxyl groups on solid silica catalysts. Since that time deuterium has been employed in studies of surfaces using a variety of analytical techniques. Quartz, cristobalite and silicic acid have been studied by Harris and Rossington (4), and silica, silica-alumina, alumina, and platinum on alumina have been examined by Hall and co-workers (5, 6). Infrared spectroscopic methods have been combined with deuteration of alumina by Peri and Hannan (7). Polyphthalocyanine catalysts have been examined by Acres and Eley

(8), and by Ichikawa and co-workers (9). A number of papers (10-12) have also appeared in which deuterium exchange with aromatic alkali metal charge transfer complexes have been studied using gas chromatography as a measuring technique. Tsuda and Inokuchi (13, 14) followed the deuterium decay over a benzonitrile-cesium ion radical salt. Deuterium exchange has also been employed in the study of the surface of metals, for example, on tungsten (15). Hall *et al.* (17) and Cheselske *et al.* (16) have examined the model system of tantalum-hydrogen. Tsuchiya *et al.* (18) studied the exchange of gas phase deuterium with hydrogen preadsorbed on platinum black. Exchange of deuterium with glass has also been examined (19, 20).

The present work, in which the interaction of deuterium with the surface of boron phosphate (BP) is measured, was initiated for several reasons. Earlier studies in this laboratory (21) had suggested the existence of both Lewis and Brønsted acidic sites on the surface of BP, and recent spectroscopic studies (22, 23) provided more direct confirmatory evidence for such

sites. Deuterium exchange offers the possibility of measuring the concentration of exchangeable hydrogen atoms bound to the surface, and as shown below, can also provide information on the surface density sites bare of hydrogen which can take up deuterium.

METHODS

Two different samples of boron phosphate with phosphorus/boron molar ratios of 1.12 and 1.17 were prepared from boric acid (Fisher reagent grade) and orthophosphoric acid (Fisher reagent grade 85%) in a manner similar to that described previously (24). The two different ratios of boron phosphate are both in the range (1.0 to 1.4) studied previously (21) and in which the highest catalytic activity is obtained, while the ratios are sufficiently different so as to allow any effects of varying the phosphorus/boron to be observed.

Hydrogen (prepurified grade) and deuterium (CP grade), which were obtained from Matheson, were specified to be 99.9 and 99.5% minimum, respectively. Our analyses showed the H₂ to contain O₂, HD, and D₂ in amounts of 20 ppm, 0.25, and 0.006%, respectively. D₂ contained 1.3% HD and 2.3% H₂. Hydrogen deuteride (research grade) was obtained as 99% pure from Merck, Sharpe, and Dohme. Our analyses showed 2.7% H₂ and 0.3% D₂.

The apparatus employed consisted of a standard vacuum system to which was attached an isolatable glass loop. Contained within the glass loop was an all-glass circulatory pump, a trap, and a quartz reactor which could be maintained at constant elevated temperatures. A side arm from the loop led to an automatic pressure controller (Granville Phillips Series 213) which itself was connected to a mass spectrometer (hybrid of CEC 21-614 and 21-620A). An ionization gauge (CVC GIC-017) mounted near the mass spectrometer analyzing chamber was used to

maintain a low constant sampling pressure of $2.0 (\pm 0.2) \times 10^{-6}$ Torr.

Analyses of the concentrations of H₂, HD, and D₂, in the loop were obtained by monitoring *m/e* peaks of 2, 3, and 4. Scans beyond these ranges showed all other peaks to be of negligible size. In the calibration of the mass spectrometer for H₂, HD and D₂ mixtures, peak height ratios were compared with the known mole ratios. In all cases plots of mole ratios versus peak height ratios were linear. Calibrations were made with known mixtures of two components, and the results of these calibrations were checked against three component mixtures of known concentration. The measured concentrations of the three components agreed in all cases with the known concentrations to within $\pm 5\%$. Calibrations were checked periodically.

Aliquots of the samples of boron phosphate were pretreated at 10^{-6} Torr at a variety of temperatures and for various lengths of time (between 6 and 13 hr) in the quartz reactor. A known quantity of deuterium was introduced and the progress of the reaction was followed. Surface areas of the samples were measured both before pretreatment and after the reaction. Before pretreatment, all aliquots of the catalysts with phosphorus/boron ratio 1.12 and 1.17 had surface areas falling in the range 15.4 ± 1.0 and 8.5 ± 0.5 m²/g, respectively, while after pretreatment, the average values were 29.5 and 24.0 m²/g, respectively.

Temperatures in the range 425–468°C and initial D₂ pressures from 80 to 176 Torr were employed. Similar experiments were also performed in the absence of catalyst and the data from such experiments was applied as a correction to that obtained in the presence of the catalyst.

RESULTS AND DISCUSSION

Figure 1 illustrates the progress of a typical reaction on a sample of boron phosphate of P/B equal to 1.17, at 445°C

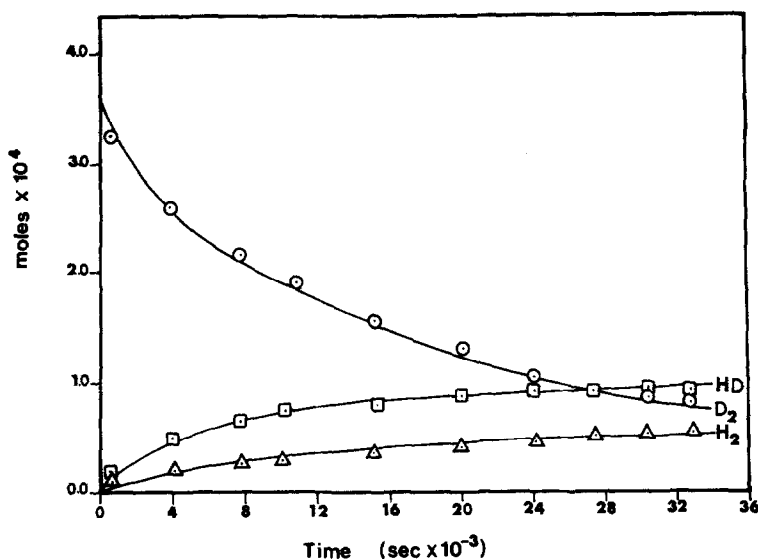
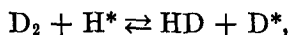
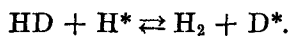


Fig. 1. Moles of gas at various times during exchange of deuterium on boron phosphate ($P/B = 1.17$) at 445°C and initial deuterium pressure of 78.0 Torr.

and an initial D_2 pressure of 78.0 Torr, for a total reaction time of approximately 10 hr. As can be seen from Fig. 1, the amount of D_2 lost from the gas phase (2.7×10^{-4} moles) does not equal the quantity of HD gained by the gas phase (1.0×10^{-4} moles). This suggests that the reaction,



where the asterisk refers to a surface species is unlikely to be the sole reaction. A small amount of H_2 is also produced which may tentatively be ascribed to the reaction,



In all cases the rate of change of the moles of D_2 in the gas phase (blank corrected) plotted versus the moles of D_2 was found to be linear, except for a slight curvature shown at the beginning (first 30 min) of the reaction. The use of the differential form of the first order rate equation circumvented the problem associated with apparent lack of attainment of equilibrium even after 10 hr of reaction time. Table 1 (column 4) records

the absolute rate constants calculated from the decay of the concentration of D_2 . From these data an apparent activation energy of $9.5 (\pm 1.5)$ kcal mole⁻¹ was obtained for the BP sample with P/B equal to 1.17. Limited data were employed to obtain a value of $0.8 (\pm 0.2)$ for n' , the external order of the reaction, where the pressure dependence of the absolute rate constant was assumed to follow the Freundlich equation. Although direct comparison with data from the literature is difficult because of the lack of detailed kinetic studies of deuterium exchange on oxides, it is of interest to note that results obtained by Hall *et al.* (17) for the Ta-H system gave an activation energy for the exchange process of 14.9 kcal mole⁻¹ and rate constants of 5.0×10^{-4} to 2.8×10^{-3} sec⁻¹ over a temperature range of 530 to 640°C . The rate constants given in column 4 of Table 1 correspond to values in the range from 0.2×10^{-4} to 1.8×10^{-4} sec⁻¹. While no claim is made that any direct relationship exists between the two systems, these results compare reasonably well with the present values.

Since measurable quantities of HD are produced when D₂ is contacted with BP, the rate of formation of HD was also examined and found to be first order with respect to the concentration of HD in the gas phase. In all cases the surface area employed in the calculations was that measured after completion of the reaction. Separate experiments showed that, although the surface area increased during the pretreatment of the catalyst, little or no change occurred during the reaction itself. The rate constants obtained from the HD concentration data produced an apparent activation energy of 14.2 (±1.5) kcal mole⁻¹ and an external order, *n'* of 0.9 (±0.2), similar in magnitude to that obtained from the D₂ decay data.

From the blank corrected concentration data it was possible to calculate the net loss of deuterium atoms from the gas phase. Presumably, deuterium atoms may be lost from the gas phase by one or both of two processes, exchange with surface hydrogen atoms, and chemisorption on "empty" sites. The calculation of deuterium lost from the gas phase, or conversely, deuterium gained by the surface, was made on the basis of a mass balance,

$$[D^*] = 2[D_2]^0 - (2[D_2]_\tau + [HD]_\tau),$$

where $2[D_2]^0$ represents the total initial moles of deuterium atoms, and the number of moles of deuterium atoms present in the gas phase at time τ is given by $(2[D_2]_\tau + [HD]_\tau)$. $[D^*]$ is the number of moles of deuterium atoms gained by the surface. All quantities are expressed per unit area of catalyst, and have been blank corrected. Figure 2 illustrates a plot of $[D^*]$ versus time for a typical reaction. A reasonably smooth, monotonically increasing, but in most cases, eventually leveling curve was obtained with all reactions.

Although the present work does not involve the chemisorption of deuterium in the usual sense, nevertheless, the quantity $[D^*]$ does represent the net loss of deuterium to the surface, and as such could be construed as approximating a chemisorptive process. With this in mind the data for $[D^*]$ versus time were treated against the integrated Elovich equation for the various reactions. The resulting plots (with $\tau_0 = 0$) were all linear over a large region of $\ln \tau$ but convex to the abscissa for small values of τ . Completely linear plots were obtained by optimization of τ_0 .

The observed gain of deuterium atoms by boron phosphate may occur as a consequence of an exchange of deuterium with

TABLE 1
Absolute Rate Constants Calculated from Decay of Gas Phase D₂ Concentration
and from the Increase in Gas Phase HD Concentration

Catalyst P/B (mole/ mole)	Initial D ₂ pressure (Torr)	Reaction temperature	Rate constant		$[D^*]_{\max}$ (mole m ⁻²) (×10 ⁵)	$[\Delta H^*]_g(\max)$ (mole m ⁻²) (×10 ⁵)	S _E (mole m ⁻²) (×10 ⁵)
			$k_m^{D_2}(\times 10^{15})$ (mol. sec ⁻¹ m ⁻²)	$k_m^{HD}(\times 10^{15})$ (mol. sec ⁻¹ m ⁻²)			
1.12	88.3	733	3.49	5.16	1.04	1.00	0.04
1.12	69.0	753	2.31	—	1.26	0.90	0.36
1.17	80.9	698	2.63	4.19	0.59	0.16	0.43
1.17	177.0	736	6.40	9.11	2.12	1.25	0.87
1.17	124.0	741	5.91	6.09	1.00	0.85	0.15
1.17	78.0	704	1.52	3.50	0.34	0.20	0.14
1.17	75.3	623	0.98	0.87	0.41	0.46	≈0
1.17	80.0	739	3.34	4.54	1.92	1.20	0.72
1.17	78.0	718	2.78	4.38	2.18	0.65	1.53

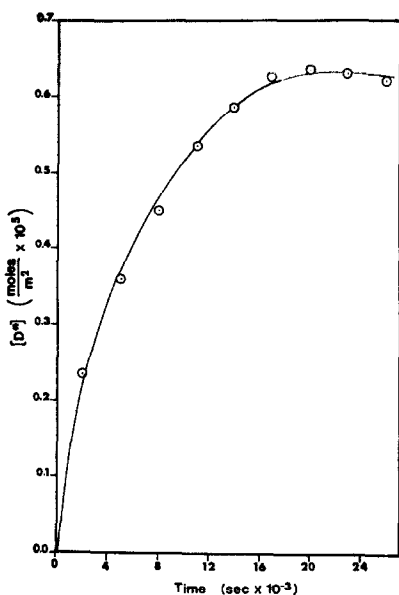


FIG. 2. Calculated moles of deuterium atoms gained by surface, $[D^*]_t$, vs time during exchange with deuterium at 425°C and initial deuterium pressure of 80.9 Torr.

surface hydrogen, and/or the occupation of an empty surface site, that is, one which is bare of hydrogen. The amount of deuterium gained by the surface ($[D^*]$), therefore is an indicator of the total number of active sites for a given temperature and pressure. The maximum values of deuterium gained by the surface ($[D^*]_{\max}$) are shown in column 6 of Table 1. In general, $[D^*]_{\max}$ increases with temperature for both catalysts. With the catalyst of P/B equal to 1.17 the amount of surface deuterium is approximately constant for low temperatures (623–700°K) at a value of 0.4×10^{-5} mole m^{-2} , but rises to 2.1×10^{-5} mole m^{-2} between 700–750°K.

It seems a reasonable assumption that D_2 exchange with surface hydrogen would result in the appearance of this hydrogen in the gas phase as HD or H_2 . The increase in the gas phase concentration therefore provides an indication of the amount of surface hydrogen which is exchangeable under the specific conditions of a given

reaction. The amount of hydrogen gained by the gas phase can be obtained from

$$\Delta[H^*]_g = 2[H_2]_t + [HD]_t - (2[H_2]^0 + [HD]^0),$$

where $\Delta[H^*]_g$ represents the surface hydrogen atoms taken into the gas phase, $2[H_2]_t + [HD]_t$ is the total number of gas phase hydrogen atoms at time t , and $2[H_2]^0 + [HD]^0$ the total number present initially. In the present work the initial quantities of H_2 and HD in the gas phase are negligible and the equation reduces to

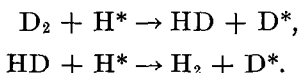
$$\Delta[H^*]_g = [HD]_t + 2[H_2]_t.$$

Calculated values of $\Delta[H^*]_g$ for each reaction in all cases increased with time, as the reaction progressed. Maximum values obtained for $\Delta[H^*]_g$ for each of the reactions are shown in column 7 of Table 1. The quantity of hydrogen held by the surface, which ranges between 1.2×10^{14} and 7.5×10^{14} atoms/cm², depending upon the experimental conditions, compares closely with data reported in the literature on other acidic catalysts. Hall and co-workers (5, 17) reported surface densities of hydroxyl groups of between 1.5×10^{14} and 4.5×10^{14} molecules/cm² on silica catalysts, while Harris and Rossington (4) found OH concentrations of 3.85, 2.52, and 2.29×10^{14} molecules/cm² for quartz, cristobalite, and silicic acid, respectively.

The exchange mechanism may or may not require an empty site; nevertheless, the number of sites active for exchange is presumably reflected in the $\Delta[H^*]_g$ values since the exchange process will generate additional gas phase hydrogen. On the other hand, $[D^*]$ is believed, under a given set of conditions, to represent the total number of sites for taking up deuterium. In principle, then, the difference between these two should provide an estimate of those empty sites (S_E) where only chemisorption takes place. The values of S_E are given in column 8 of Table 1. In all but two reactions $[\Delta H^*]_{g \max}$ is greater

than S_E , which implies that, in general, for both samples of boron phosphate, the number of active hydrogen atoms on the surface is larger than the number of empty sites which are active for chemisorption alone. Further, values of $S_{E \text{ max}}$ for BP of P/B ratio equal to 1.17 increase with increasing temperature, presumably indicating the increase in number of deuterium atoms of the gas phase which have sufficient energy to overcome the activation energy of chemisorption onto empty sites as temperature is increased. Although data on BP of P/B equal to 1.12 is limited, nevertheless if reactions under similar conditions are compared for the two catalysts, it appears that $S_{E \text{ max}}$ values are somewhat larger for catalyst of P/B 1.17 than for catalyst of P/B equal to 1.12.

In summary, deuterium reactions on BP in the temperature range of 623 to 741°K resulted in the production of HD and H_2 in the gas phase in proportions of approximately 2:1. Hence, the existence of exchangeable hydrogen atoms on the surface of BP is demonstrated, although no claim for complete exchange can be made. The data presented also suggest that in addition to exchange of deuterium with surface hydrogen, some gas phase deuterium remains on the surface on "empty" sites which in some cases appear to be as many in number as surface hydrogen atoms. Although the present data do not permit detailed mechanistic conclusions to be drawn, nevertheless the production of both HD and H_2 imply the occurrence of at least two reactions, possibly



The demonstration of the existence of a substantial number of empty sites might be taken to suggest that an empty site mechanism for the exchange cannot be precluded.

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