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Hydrogen Spillover on Platinum–Alumina, Effect of Water

During the course of experimental work involving the adsorption of hydrogen on platinum–alumina, an unexpected phenomenon was observed. This phenomenon is described below and an explanation involving hydrogen spillover is offered which fits the experimental observations reasonably well. (See Ref. (*1*) for an extensive review of hydrogen spillover, and (*2*, *3*) for later studies of interest. Also, the work of Levy and Boudart, Ref. (*4*), especially for evidence of water as a promoter.)

In the experiments in question, a crushed and sieved (through 40 on 50 mesh) sample of catalyst was loaded into a $\frac{1}{4}$ in. diameter stainless steel tube. The catalyst was degassed in argon at 480°C, reduced in hydrogen at that temperature, and then brought to its final temperature of 150°C in a flow of hydrogen. A pulse of HD containing an argon tracer was admitted and the retention time measured. Figure 1 shows a schematic of the setup and the chromatogram observed.

Retention time was, as expected, roughly linear with platinum content of the sample. However, it was also observed that when water or oxygen was injected as a pulse, the retention time of subsequent HD pulses increased. Once water or oxygen was added, the new, longer retention time remained constant for subsequent HD pulses for up to an hour or more. The slope of the retention time versus added water curve was independent of platinum level (see Fig. 2). At very high platinum levels, there appeared to be an agglomerating effect, additional platinum content not producing substantial further increase in HD retention time.

It seems clear that hydrogen spillover is responsible for these observations. Without platinum, there is no effect. With substantial platinum present, the effect is proportional to injected water, and water is known to facilitate hydrogen spillover.

It is inferred that injected water is adsorbed onto the alumina surface where it hydrolyzes Al–O bonds to produce surface hydroxyl groups. Independently, H atoms present on the platinum surface migrate to specific, nearby spillover sites on the alumina surface. However, the presence of the hydroxyls on the alumina provides bridges by which H atoms can migrate over the alumina surface to occupy sites previously inaccessible to them. Thus, the total amount of spilled-over hydrogen is increased by the injected water. Since the spillover hydrogen does not exchange directly with the gas phase, the only way for it to return to the gas is by migrating over the alumina surface until it finds a platinum crystal from which it can recombine and desorb. Thus, any increase in spillover hydrogen will be bound to cause an increase in retention time, since it takes time for the spillover hydrogen to migrate.

From the data, it is inferred that a mechanism such as the following is involved (superscript (^{0}) indicates zero valent spillover hydrogen site)

$$\mathrm{HD} + \mathrm{HPt} \rightleftarrows \mathrm{DPt} + \mathrm{H_2} \qquad (1)$$

$$\mathrm{DPt} + \mathrm{H^0O{=}S} \rightleftarrows \mathrm{HPt} + \mathrm{D^0O{=}S} \quad \text{(spillover)} \qquad (2)$$

$$\mathrm{DPt} + \mathrm{HO{-}S} \rightleftarrows \mathrm{HPt} + \mathrm{DO{-}S} \qquad (3)$$

$$\mathrm{DO{-}S} + \mathrm{H^0O{=}S'} \rightleftarrows \mathrm{HO{-}S} + \mathrm{D^0O{=}S'} \qquad (4)$$

where HO–S represents hydroxyls on the alumina surface formed by reaction of water with the dehydrated surface. Also, $\mathrm{H^0O{=}S}$ represents spilled-over H atoms

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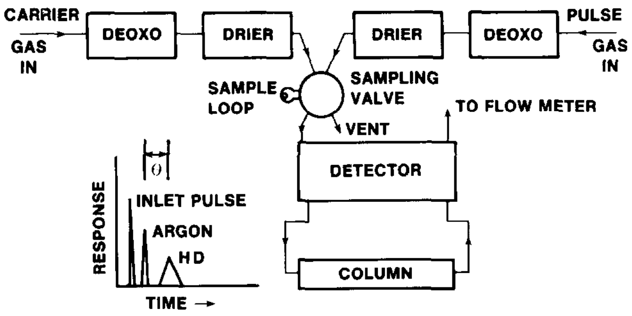

FIG. 1. Schematic diagram of chromatogram and experimental setup.

on the alumina surface. It is further assumed that the hydroxyls produced on the alumina surface by the water are so located that additional spillover sites are made accessible.

Of course, in these experiments, equilibrium does not exist nor even a steady state situation. Whatever net effect takes place at the leading edge of the HD pulse will be reversed at the trailing edge. Thus, any calculations concerning the passage of the HD pulse through the column had to be done on the basis that all events are transient phenomena.

Rate expressions can be written for the above reactions in the usual way except that the rates will be both time and position dependent. Constant carrier flow was assumed. Thus, location of the pulse is a linear function of the elapsed time.

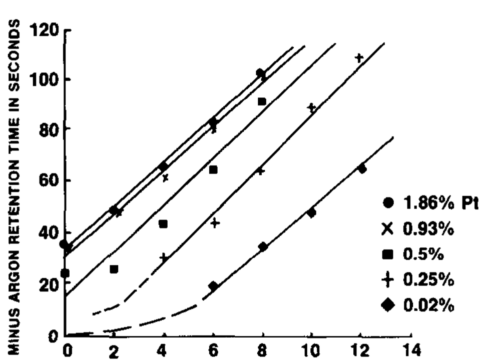

FIG. 2. Effect of added water on HD pulse retention by platinum on alumina catalysts.

The rate expressions are as follows:

$$
\begin{aligned}
R_{1x} &= k_1[\mathrm{HD}]_x[\mathrm{HPt}]_x\\
R_{-1x} &= k_{-1}[\mathrm{DPt}]_x[\mathrm{H_2}]_x\\
R_{2x} &= k_2[\mathrm{DPt}]_x[\mathrm{H^0O{=}S}]_x\\
R_{-2x} &= k_{-2}[\mathrm{HPt}]_x[\mathrm{D^0O{=}S}]_x\\
R_{3x} &= k_3[\mathrm{DPt}]_x[\mathrm{HO\text{-}S}]_x\\
R_{-3x} &= k_{-3}[\mathrm{HPt}]_x[\mathrm{DO\text{-}S}]_x\\
R_{4x} &= k_4[\mathrm{DO\text{-}S}]_x[\mathrm{H^0O{=}S}]_x\\
R_{-4x} &= k_{-4}[\mathrm{HO\text{-}S}]_x[\mathrm{D^0O{=}S}]_x
\end{aligned}
$$

where x represents a particular location in the column.

Boundary conditions are simply that at time = 0, all deuterated species have zero concentration, all platinum surface is H saturated and the HO concentration is equal to twice the amount of water injected. The initial $[\mathrm{HD}]_0$ is, of course, known from the amount injected into the column. The column was assumed to be radially uniform but expressions for axial dispersion were included as well as the effects of mass flow.

In the absence of significant amounts of adsorbed water, the retention of an HD pulse is caused mainly by the depletion of HD at the leading edge of the pulse by reactions (1) and (2). The reverse reactions (−1) and (−2) then occur at the trailing edge of the HD pulse. Thus, the HD pulse gradually falls behind the argon tracer pulse as they both pass through the column. This effect naturally increases with increasing platinum surface exposed to the gas. When water is injected, it adsorbs on the alumina surface, producing and/or exposing hydroxyl groups. These do not exchange with the hydrogen gas but do exchange with adjacent OH groups, with adsorbed H atoms on the Pt surface, and with spillover H atoms if they are adjacent to them on the surface. Thus, when subsequent HD pulses are injected, the following sequence takes place. At the leading edge of the pulse, reactions (1) and (2) occur. This is followed by reactions (3) and (4), always involving only spatially adjacent entities. The D atoms, in effect, migrate away from the Pt across the alumina surface by these reactions. Finally, at the trailing edge of the pulse, the HD in the gas is replenished by reversal of all reactions. In effect, the pulse is delayed and axially dispersed because of the time necessary for these successive steps to occur. Thus, a forward and reverse surface migration of D atoms away from and later back toward the platinum crystallites delays the HD pulse more than it would have been delayed in the absence of the water. All of this was incorporated into a computer program which calculated the retention time as a function of platinum surface and water content of the column. The program also calculated and plotted the appearance of the expected chromatogram.

The model was found to reproduce the major features of the observations based on the proposed mechanism and to be compatible with equilibrium constants of the order of magnitude of unity for the four equations provided that the following assumptions were made: first, that the number of spillover sites on the dry surface was taken as approximately equal to the number of platinum atoms (high dispersion assumed); and second, that the number of new spillover sites generated or made accessible by the injected water was approximately equal to the amount of water injected. An assumption similar to the second one above has previously been suggested in Ref. (*4*).

Thus calculated, retention times versus added water plots were linear and parallel in agreement with experiment. Also, calculated and plotted GC peak width broadened with increasing added water as in the experiments. At low platinum and water levels, added water had much less effect so that there is a decided curvature to the plots (dashed lines in Fig. 2). Data obtained on samples other than those plotted is fragmentary but shows the curvature indicated. No retention times shorter than that of the argon tracer were observed or calculated. The suggested explanation of this curvature is as follows: reactions (3) and (4) can occur only if the species involved are adjacent to one another. Thus, substantial occurrence of these reactions requires "pools" of adjacent hydroxyls contiguous with a platinum crystallite. This occurs only with low probability when both platinum and water levels are low.

It is also clear that direct exchange between gaseous HD and surface hydroxyls does not take place to any appreciable degree, since there is no retention of the HD pulse unless Pt is present on the catalyst whether H_2O (or O_2) is introduced or not.

It is concluded that the proposed mechanism is the one involved in the spillover phenomenon.

In this brief study, the important point we would like to emphasize is the previously unreported observation regarding the effect of water on the HD retention time and the possible value of measurements of this type in the study of the interaction of hydrogen with certain catalyst surfaces. For a more complete study, of course, the effects of temperature, pressure, flow rate, dispersion, and support surface area ought also to be studied. The authors feel that such more detailed studies cannot fail to shed additional light on these phenomena.

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