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A Pulse Flow Microreactor Study of Hydrogen Spillover from Palladium on Carbon to Silica and Polyvinylphenol

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A portion of the hydrogen of a high-surface-area silica was exchanged with deuterium gas in a pulse flow microreactor. The exchange reaction was rapid at 190°C when the silica was physically mixed with a Pd on carbon catalyst. The amount of readily exchangeable hydrogen was determined using a titration technique to be 0.87 mmol H/g silica, more than 50% of the estimated number of hydroxyl groups. A smaller number, 0.46 mmol H/g silica, was determined after the silica was partially dehydrated by heating to 360°C. Although silica itself becomes an active catalyst for H_2/D_2 exchange after being heated to 360°C, exchange between D_2 gas and the surface hydroxyls was not observed in the absence of the Pd/carbon catalyst. The results are interpreted in terms of hydrogen spillover from the Pd/carbon catalyst to the silica surface. Equilibrium is established for a pool of hydrogen including that in the gas phase, on the catalyst surface, and a certain portion of the hydrogen on the surface of the silica, providing evidence that transport by spillover is rapid in comparison to the transit time of a pulse, about 3 min. Similar results were found by substituting polyvinylphenol for silica. The results illustrate that ready pathways exist for transport of spillover hydrogen between solid substrates and physically admixed catalyst. © 1997 Academic Press

INTRODUCTION

The transport of activated hydrogen from a catalytic surface to a solid substrate is a key step in a number of important processes. Basic information about the nature of such transport mechanisms is relevant to those hydroprocessing technologies where the molecular motion of nondistillable substrates, for instance coal or heavy residua of petroleum, is limited. However, more information on the important role played by the transport of activated hydrogen from a catalyst surface to substrates of limited physical mobility in hydrocarbon conversion chemistry is coming to light. For example, model compounds rendered immobile by covalent bonding to a high-surface-area silica have been used to demonstrate that a dispersed, sulfided Mo catalyst promotes hydrocracking reactions in the solid state under high pressure (1).

Previous investigations in this laboratory have made use of hydrogen/deuterium exchange reactions to demonstrate the transport of hydrogen from an MoS_2 catalyst to coal (2) and from a Pd/carbon catalyst to coal (3). The present investigation was undertaken to continue these investigations of hydrogen transport from catalysts to substrates of restricted molecular mobility by using either of two well-defined solid substrates, a fumed silica or polyvinylphenol, and a well-known and preactivated catalyst, palladium on carbon. Although these two substrates are unlike coal in most regards, all three share one common aspect in that they have a significant number of −OH groups.

The importance of spillover to heterogeneous catalysis has been underscored by a recent review (4), which concludes that further studies of the transport mechanism between surfaces in physical contact are needed. The surface of silica has been the subject of several investigations into the transport of spillover hydrogen. A key study in relation to the work reported here contained an experiment in which the platinum-catalyzed exchange of gas-phase deuterium with hydrogen in the SiOH groups of a high-surface-area silica was monitored by infrared spectroscopy (5). Deuterium was observed to migrate over a distance of nearly 1 cm from a single piece of platinum metal resting on a disc of silica. Direct observation of the substitution of the infrared band of SiOD for SiOH positively identified the hydroxyl group as the site of exchange. Similar conclusions were reached in another study based on the infrared technique, this time using palladium on silica (6). In addition to observing the simple exchange reaction with surface hydroxyl groups, the latter study also demonstrated that migrating hydrogen atoms could be trapped with a stable free radical (DPPH). This important observation provides positive evidence that spillover of hydrogen atoms from palladium followed by their transport over the surface of silica may result in a true chemical reduction.

Direct evidence for hydrogen spillover was reported by Wu *et al.* (7) in a study of ruthenium supported on silica. They found a significant difference between the total

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amount of hydrogen taken up by ruthenium on silica as measured by chemisorption versus the amount taken up only by ruthenium as measured by nuclear magnetic resonance (NMR) spectroscopy. They also used NMR to observe deuterium on the ruthenium surface exchange with the hydrogen of SiOH groups at room temperature. In a subsequent study (8) it was shown that hydrogen spillover from ruthenium to its silica support can interfere with the accurate evaluation of the dispersion of the metal when measured by the volumetric hydrogen chemisorption technique. When all of the reports are taken together it is clear that the existence of spillover from a noble metal to the surface of silica is well established and that several aspects of the mechanism are understood.

Other chemistry that has been attributed to hydrogen spillover includes the activation of silica (9, 10). Silica was brought into physical contact with a platinum catalyst and exposed to hydrogen during the activation step. After the platinum catalyst was removed, catalytic activity was observed for hydrogen/deuterium exchange and for hydrogenation of an olefin. The catalysis was attributed solely to the action of activated silica. In turn, activation of the silica was attributed to the action of hydrogen spilled over from the platinum.

We have demonstrated that the silica used in the present experiments also can be activated by a simple thermal process that does not require either hydrogen or a noble metal catalyst (11). Activation resulted from heating the silica above 320°C for 16 hr in a stream of dry argon. Silica activated in this way was found to catalyze the exchange between mixtures of hydrogen and deuterium gas and to catalyze the hydrogenation of ethene. The generation of hydrogenation activity by this simple treatment has been confirmed and further illustrated with other substrates such as stilbene and naphthalene (12).

The pulse-flow microreactor experiments described below illustrate other aspects of hydrogen spillover from a noble metal catalyst to silica and to a polymer. They also reveal that in comparison to Pd on carbon, the active sites generated on silica by simple thermal treatment (11) are far less able to promote spillover.

METHODS

The pulse-flow microreactor has been described previously (2). Briefly, samples were packed in a Vycor tube (150 mm × 6 mm o.d.) equipped with Teflon endcaps, then connected to a gas manifold. Argon was used as a carrier gas at a flow rate of 6.0 ml/min unless specified otherwise. Pulses of hydrogen or deuterium were injected into the carrier stream by means of a six-port valve and a 200-μl injection loop. The sample bed was heated by a clamshell oven. The effluent gas was continuously sampled by a capillary tube leading to the inlet of a quadrupole mass spectrometer (Ametak MA100M). The amounts of H_2, HD, and D_2 were determined quantitatively by integration of the areas under their peaks. Response factors were obtained using injections of known amounts of the gases. When it was desired to pass a mixture of the gases through the reactor, an essentially simultaneous pulse of hydrogen and deuterium could be created by switching gases and making a second injection within 15 sec. The width at half-height of a typical peak observed at the exit of the reactor is about 3 min, so the resultant areas of simultaneous pulses overlap by greater than 95%. Similarly, double injections of a single gas were used to provide a pulse of twice the normal size.

The silica was a high surface area (200 m^2/g) fumed silica from Cabot Corporation (Cab-O-Sil M5). Polyvinylphenol (Cat. No. 16642, M.W. = 30000) was obtained from Polysciences, Inc. The catalyst was 10% palladium on carbon obtained from Eastman Kodak (6633). Gases were high purity, Ar (99.999%, Qualitech Gas Products), hydrogen (99.999%), and deuterium (99.999%, MG Industries). They were passed through a train of drying tubes before entering the reactor.

In a typical experiment, 0.600 g silica was mixed with 0.090 g catalyst (9 mg Pd) by grinding using a mortar and pestle. The mixture was packed in the reactor tube and held in place with quartz wool plugs. The bed was heated to 190°C within about 30–35 min under a flow of argon and held at this temperature for 16 hr to remove physically adsorbed water. The gas flow was then switched to hydrogen (4.0 ml/min) for 0.5 hr to ensure that the catalyst was reduced. Argon flow was reinstated and a sequence of hydrogen pulses was begun. A reproducible pulse size was immediately established—an indication that the reactor bed was fully reduced and ready for exchange experiments with deuterium pulses.

RESULTS

Pd/carbon alone. The basic techniques used in the pulse-flow microreactor experiments closely follow those established in previous investigations of the exchange between deuterium gas and hydrogen bound to coal catalyzed by either MoS_2 (2) or Pd/carbon (3). As described later, the exchange reaction between deuterium gas and the high-surface-area fumed silica was observed after it was physically mixed with the Pd/carbon catalyst. The experiments described now were performed to establish that the exchange reaction reflected the activation of hydrogen on the catalyst surface followed by its transport to the silica surface. First, pulse shapes and response factors were established by making separate injections of known amounts of deuterium and hydrogen using an empty reactor under reaction conditions. Sampling conditions were adjusted to make the response factors for D_2 and H_2 equal. Next, simultaneous pulses of hydrogen and deuterium were injected. As expected, the very small amount of HD present in the reactant gases did not increase, confirming that the exchange reaction did not occur without catalyst.

To determine that the amount of catalyst used in the spillover experiments had sufficient activity, the reactor was packed with 0.090 g of Pd/carbon, the same amount used with silica as described below. Before exchange experiments were carried out, the catalyst was reduced by passing a stream of hydrogen through the reactor. After switching back to argon carrier gas, a series of simultaneous pulses of hydrogen and deuterium was begun at 190°C. It was apparent that the exchange reaction went to completion from the relative amounts of H_2, HD, and D_2 observed. The amounts of H_2, HD, and D_2 obtained by integration of the areas under the peaks were in the same proportions as expected from the published equilibrium constant (13). However, the mixture of gases that emerged from the reactor after the first simultaneous pulse of H_2 and D_2 was enriched in hydrogen. This imbalance was caused by the equilibration of the pulse gases with the hydrogen retained by the catalyst from the initial reduction step. After several injections of the gas mixture, the amounts of hydrogen and deuterium recovered after each simultaneous pulse eventually became equal. After reaching this steady state, it was assumed that equimolar amounts of hydrogen and deuterium were retained on the catalyst surface. These results verify that the amount of catalyst used in the typical exchange experiment is sufficient to activate and bring to equilibrium the volumes of hydrogen and deuterium used under simultaneous pulse conditions.

Pd/carbon with silica. The high-surface-area silica chosen for these hydrogen spillover studies was the same material we used previously in work that demonstrated that simply heating it to 320°C in a stream of dry argon was sufficient to generate sites capable of catalyzing exchange between H_2 and D_2 present in the gas phase. Although activation required higher temperatures, the exchange between the gases was observed at temperatures below 200°C once the catalytic sites had been generated. The choice of reaction temperature for the present spillover studies with silica, 190°C, was made with two considerations in mind. First, the exchange reaction should be rapid relative to the time frame of the pulse experiment. Second, the generation of catalytic activity on the surface of silica itself should be avoided at least in the initial experiments. To avoid introducing complications from a second source of catalytic activity, samples used in the initial set of experiments were never heated to the temperature required to create catalytic activity on silica. Accordingly, it is presumed that Pd/carbon was entirely responsible for the activation of hydrogen.

A physical mixture of 614 mg silica with 102 mg palladium on carbon (10.2 mg Pd) was packed in the reactor, heated within 35 min to 190°C under a flow of argon, and held at this temperature for 16 hr to remove physically adsorbed moisture. The gas flow was changed to hydrogen (4.0 ml/min) for 0.5 hr to reduce the catalyst, then changed back to argon. A series of hydrogen pulses was then injected to confirm that the catalyst was fully reduced. The area of each pulse in the series was the same, verifying there was no net uptake or release of hydrogen. A series of deuterium pulses was then begun to investigate the hydrogen/deuterium exchange reaction.

Injection of the initial pulse of deuterium resulted in a spectrometer response due almost exclusively to hydrogen (Fig. 1a). The overwhelming preponderance of hydrogen observed following the first deuterium pulse indicated that the pool of exchangeable hydrogen was quite large relative to the amount of D_2 (19.6 μmol) in the pulse. The total number of moles of gas in the exit pulse was in close agreement with the moles of D_2 injected, showing that there was no detectable gas uptake, merely an exchange. The initial pulse was followed by a series of deuterium pulses at intervals of roughly 8 min. A gradual reduction in the relative

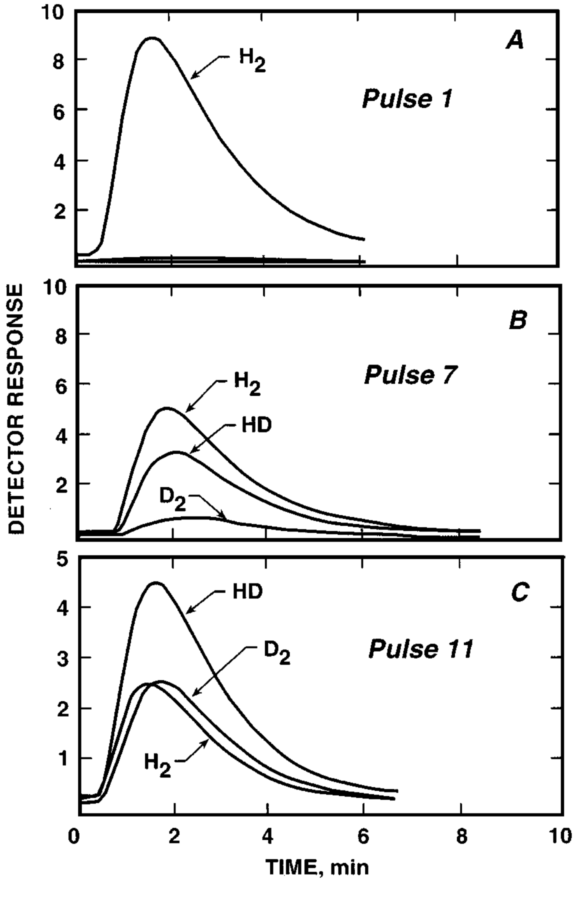

FIG. 1. Three stages during the estimation of the exchange pool size of a mixture of 0.614 g silica and 0.102 g Pd on carbon using the titration technique. Pulses of 19.6 μmol D_2 were obtained by the double injection technique. The composition of the exit pulses changes throughout the series with a progressive increase in the areas under peaks for D_2 and HD relative to H_2. Hydrogen removed from the sample is equivalent to essentially the entire amount of pulse 1, 72.6% of pulse 7, and 49.2% of pulse 11. The areas for H_2, HD, and D_2 in pulse 11 represent 25.2, 48.0, and 26.8% of the total, respectively.

amount of hydrogen and corresponding increase in deuterium was observed in the exit stream with every pulse in the progression. The trend is illustrated by comparison of the seventh pulse with the first (Fig. 1). For each pulse, the relative amounts of H_2, HD, and D_2 were in the proportions expected from the equilibrium constant. It thus appears that every pulse comes to equilibrium with a pool of hydrogen including that in the gas phase, on the catalyst surface, and the amount available for rapid exchange on the silica. Equimolar amounts of H and D emerged from the reactor on reaching pulse 11 (Fig. 1c). From this trend, it was apparent that the hydrogen pool was limited in size and could be effectively depleted by repetitive pulses.

A suitable method was required to measure the size of the pool of exchangeable hydrogen. Summation of the hydrogen removed by continued pulsing with deuterium until the pool was exhausted was impractical because the relative amount removed by each successive pulse slowly approached zero as the isotopic dilution progressed. Rather than estimate the endpoint in this way, a simple method to determine the size of the exchange pool was based on the following titration technique. For the sake of convenience and ready recognition, the pulse that returned equimolar amounts of hydrogen and deuterium was taken as the endpoint. At this point, 50% of the exchangeable hydrogen had been removed. The total amount of hydrogen, HD, and deuterium obtained from the beginning of the titration to this endpoint was found by summing the respective areas from all of the individual pulses. The amount of H released, expressed as a fraction of the total moles of gas in all the pulses, is

$$\frac{\mathrm{H}}{\mathrm{H}+\mathrm{D}} = \frac{\sum \mathrm{H}_2 + \frac{1}{2}\sum \mathrm{HD}}{\sum \mathrm{H}_2 + \sum \mathrm{HD} + \sum \mathrm{D}_2}.$$

For the titration illustrated in Fig. 1, this fraction was 0.700. Multiplication of this fraction times the total number of moles of gas injected up to the 50% end point gave a value of 301 μmol of hydrogen released. The total size of the exchange pool on the catalyst and silica combined was twice this value, or 602 μmol H.

The exchange reaction was reversible and the titration reproducible. Reversibility was demonstrated by the complete removal of the deuterium incorporated into the catalyst/silica mixture during the first titration by passing a flow of pure hydrogen through the reactor for several hours. After the flow of argon was reinstated, the titration procedure was repeated as before. The second titration was comparable to the first in every way, and the values found for the amount of exchangeable hydrogen were in excellent agreement. In general, the reproducibility of the values calculated for the exchange pools is estimated to be within 10%. Values for several examples are given in Table 1.

The initial experiments using the Pd/carbon catalyst alone gave evidence that it retained a measurable amount of hydrogen after its reduction prior to titration. The size of the exchange pool on the catalyst alone was determined by the same titration method using nearly the same amount, 90 mg, as in the experiment with silica. The endpoint was reached in 3 pulses, equivalent to an exchange pool of 9 mmol H/g Pd. This value is identical to that determined earlier (3) using a sample of the same catalyst in a somewhat larger amount (400 mg) that allowed for greater precision. This earlier work also established that the titration could be reproduced in the reverse direction by first saturating the catalyst with deuterium, then titrating with hydrogen. The average value reported was based on eight determinations, four from each direction. When the size of the exchange pool is expressed as an atomic ratio, H/Pd = 1. Although the dispersion of Pd is not known, it seems unlikely to be as high as 1. It is more likely that a portion of the hydrogen retained by Pd/carbon resides on the carbon surface as a result of spillover from the catalytic metal.

TABLE 1

Titration of Samples with Deuterium

Sample	Weight (mg)	Temperature (°C)	Pulses to 50% endpoint	Titratable H (mmol/g)	
				Total sample	Substrate[a]
Pd/carbon	90	190	3	90	9
Silica–Pd/carbon	600/90	191	22[b]	1.0	0.87
		360	13[b]	0.59	0.46
Polyvinylphenol–Pd/carbon	101/75	135	25.5[b]	0.70	6.30

[a] mmol H per g Pd, silica, or polyvinylphenol, respectively. Moles expressed in terms of atomic hydrogen.

[b] Average of duplicate determinations.

The size of the pool of exchangeable hydrogen on silica alone was calculated by subtracting the value for Pd/carbon from the total. For the experiments at 190°C, the pool on silica was equivalent to 0.87 mmol H/g silica.

By its nature, the hydrogen available for exchange on silica is almost exclusively due to surface Si–OH groups. At the temperatures used for the titrations, physically adsorbed moisture has been removed. However, it is well known that the surface of silica may be dehydrated further by heating to still higher temperatures. When the temperature of the microreactor was raised to 360°C, water released from the silica was detected as a transient increase in the response at mass 18. The origin of the water lost at these temperatures has been assigned to the condensation of hydroxyl groups (14). It has been recently found that geminal hydroxyl groups are particularly labile during dehydration (15). We have reported that this loss of water is coincident with the activation of silica (11). Although the activated silica was able to catalyze the exchange between a mixture of H_2 and D_2 in the gas phase, when a pulse of D_2 alone was passed through the reactor, measurable amounts of HD were not produced. Thus, exchange between deuterium gas and hydrogen associated with the hydroxyls remaining on the silica surface after partial dehydration was apparently too slow to be detectable under the pulse-flow conditions used in these experiments.

In contrast to the results obtained with just silica in the reactor, the remaining hydroxyl groups do undergo exchange in the presence of Pd/carbon. When the thermal activation procedure was carried out and titration conducted at 360°C with Pd/carbon admixed with the silica, a value of 0.46 mmol H/g silica was obtained for the exchangeable hydrogen. Thus, the value obtained at 360°C is roughly 53% of that obtained at 190°C, consistent with a partial loss of surface hydroxyl groups through dehydration on heating. Furthermore, the result reveals that there is a fundamental difference between the active sites of the Pd/carbon catalyst and the sites generated on silica by thermal activation. Exchange via spillover is possible with the former even though part of the surface network of Si–OH groups has been lost, but exchange is not rapid enough to be detectable through the catalytic sites generated on the silica surface itself by thermal activation.

Pd/carbon with polyvinylphenol. The hydroxyl network of silica is largely confined to the surface of the material. Polyvinylphenol was selected to investigate a material in which the hydroxyl network exists mostly in the bulk phase. This polymer carries a much higher content of –OH groups per gram than does silica. Accordingly, a smaller sample size, 0.101 g, was used. The polyvinylphenol (M.W. = 30,000) was physically mixed with 0.075 g of Pd/carbon (7.5 mg Pd) and heated to 135°C for 16 hr under an argon flow of 4.0 ml/min. A lower temperature was used in this case to avoid possible complications that might arise should the polymer soften. The sample was then titrated with deuterium pulses as above. The endpoint was reached in 25 pulses. Next, the sample was saturated again with hydrogen by passing a flow of the gas through the reactor for several hours. A duplicate titration with deuterium then required 26 pulses to reach the endpoint, in excellent agreement with the first determination. The data are contained in Table 1.

DISCUSSION

The results of the titration experiments show that a certain fraction of the hydrogen on materials as different as silica and polyvinylphenol is readily accessible to exchange with gas-phase hydrogen at modest temperatures. The physical mixing of substrate and an active supported catalyst is sufficient to make this exchange possible. Similar observations of ready exchange have also been made using coal instead of silica or polyvinylphenol (2, 3). Because the contact between the catalyst and substrate is limited to that provided by physical mixing, it is apparent that hydrogen made available by activation on the catalyst surface must be highly mobile and able to migrate over a great range. Despite any impediment which may be associated with interparticle transfer, it is evident that ready pathways exist and migration of hydrogen to and over silica is facile. The exchange is reversible, and a reproducible value for the size of the exchange pool was obtained under the same reactor conditions. Although the values for the sizes of the various exchange pools are instructive, the more important result of these experiments lies in the demonstration of a ready pathway for hydrogen from catalyst to substrate.

The results obtained with the catalyst–silica mixtures may be readily interpreted in terms of exchange of the surface hydroxyl groups. In the case of silica, there is no other source of hydrogen except surface hydroxyls. Comparison of the value determined for the silica exchange pool, 0.87 mmol H/g silica, with an estimate reported (16) for its OH content, ~1.6 mmol –OH/g silica, implies that a substantial fraction of the surface hydroxyl groups participate in the exchange.

The results obtained in this study by using the isotopic exchange method are in accord with results obtained by others using spectroscopic methods. These include the direct observation of the exchange reaction between gas-phase deuterium and hydroxyl groups on silica by infrared absorption spectroscopy (5, 6) and the observation by NMR (7) of hydrogen spillover from ruthenium to its silica support. The latter work provided evidence for the presence of spillover hydrogen by the observation of a sharp decrease in the observed spin-lattice relaxation time of the silanol proton. The exchange reaction between deuterium adsorbed on ruthenium and the silanol proton was also observed. The rate of this exchange, estimated half-life of 12 hr at 294 K, was much slower than observed here, undoubtedly reflecting the lower temperature used in the NMR experiment. Wu *et al.* proposed spillover hydrogen acts as an intermediate in the exchange between the silanol proton and hydrogen adsorbed on ruthenium. Oxygen bridge groups, Si–O–Si, were postulated as binding sites of spillover hydrogen on silica. It is important to note that the quantities of the spillover hydrogen regarded as the intermediate in the exchange reaction in the NMR study (7) were determined to be at least an order of magnitude smaller than either the Si–OH content of the silica or the exchange pool determined here by the pulse-flow method. In this view, the exchange of the silanol groups is mediated by a much smaller quantity of mobile, weakly interacting hydrogen produced by spillover.

In addition to the quantitative measurement of the exchange pool, the exchange experiments provide further insight into the nature of the activated silica previously reported (11). The present results demonstrate that after using conditions sufficient to activate the silica, the hydroxyl groups that remain on its surface are still accessible to exchange, provided the Pd/carbon catalyst is admixed. Although the dehydration that is coincident with activating silica considerably reduced the total number of −OH groups, a substantial fraction of those remaining were available for exchange. Despite the decrease in their surface population density, pathways for hydrogen transfer among the −OH groups and between them and the active site on the Pd catalyst remained intact. To account for the retention of mobility reflected by the ease of the exchange reaction despite the loss of Si–OH groups, we invoke the postulate made by Wu *et al.* (7) that hydrogen transport involves transfer over silyl ether groups. Recent observations by NMR. (15) are relevant because they demonstrate that OH groups on the surface of silica are divided between a major fraction assigned to single silanol groups and a minor fraction assigned to geminal silanol groups. It was further shown that when the silica was heated geminal silanols were lost by dehydration, leaving behind an Si–O–Si bridge in close proximity to remaining silanol groups, a seemingly favorable alignment for the exchange reaction observed here with dehydrated silica.

In contrast to the ready exchange observed when Pd on carbon was admixed with silica, no exchange was observed with activated silica alone. Because the network for transporting spillover hydrogen remains intact on activated silica, the marked contrast in the ease of the exchange reaction must be due to a basic difference in the ability of the active sites of the two catalysts to place spillover hydrogen on the network.

As clearly demonstrated by the results using polyvinylphenol, the mobility of spillover hydrogen is not restricted to surfaces. The size of the pool of exchangeable hydrogen found for the polymer was 6.3 mmol H/g polyvinylphenol. The phenolic-OH content of polyvinylphenol based on its molecular formula is 8.3 mmol OH/g. Thus, roughly 75% of this value participated in the exchange reaction. This large extent of exchange could only be achieved by migration of deuterium throughout the bulk phase. Whether a still higher fraction could be exchanged by using a larger ratio of catalyst to substrate or by gaining a more intimate mixture of the two is not known. The essential feature demonstrated by this experiment is that hydrogen transport over long distances though the bulk phase is rapidly and readily achieved.

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