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Hydrogen Spillover in the Pt Black/Ce–Y Zeolite/Perylene System

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Large quantities of hydrogen are adsorbed at room temperature by cerium-Y zeolite after small amounts of perylene are deposited on physical mixtures of Pt black and Ce–Y sieve. The destruction of perylene ion radicals generated on the zeolite surface can be monitored via the ESR signal.

Perylene ion radicals act as sinks for migrating hydrogen and, in addition, serve as bridges which permit spillover of hydrogen from platinum black onto the zeolite surface. The ultimate hydrogen sink on the zeolite may be an adsorbed oxygen species.

Several recent investigations have been specificially directed to the study of hydrogen spillover (*1–3*). Although new examples or spillover are reported periodically, little has been done to clarify the mechanism of hydrogn transport or the nature of the migrating species. It is clear that in the Pt/WO_3 system the presence of water is necessary to obtain reduction at room temperature (*4*). One role of the adsorbed water may be that of a bridge between the Pt and the WO_3 particles which facilitiates the transport of hydrogen from the metal surface to the oxide surface. Similarly, in a Pt/carbon system, evidence exists that carbon dendrites act as bridges between Pt and carbon particles to promote hydrogen spillover (*2*).

Recently, we have shown that in physical mixtures of Pt black and Ce–Y sieve spillover could be monitored by purposely providing a sink for the hydrogen (*1*). The evidence indicated that the hydrogen diffuses across the oxide surface as an atomic-like species, one most easily represented by an $H^•$ radical. In this paper we provide further evidence that this species is most representative of the migrating hydrogen. Also we have found, quite surprisingly, that the zeolite itself is capable of reacting with very large quantities of spilled-over hydrogen. One of the primary roles of the adsorbed hydrocarbon then, is that of a bridge to allow the transport of large quantities of hydrogen from the platinum to various sinks on the zeolite. We present some ESR data which help to identify these hydrogen sinks.

EXPERIMENTAL

The details of the sample preparation and a description of the ESR techniques were described previously (*1*). In addition to grinding, some mixtures of platinum black and Ce–Y zeolite were prepared by gently rolling the desired amounts together until thoroughly mixed. These mixtures behaved similarly to those prepared by grinding. The physically adsorbed carbon tetrachloride solvent was removed prior to an adsorption run by evacuating the sample at ~60°C for 60 min. The amount of hydrogen taken up by the various samples was monitored via measurements of pressure change in a typical high-vacuum adsorption system incorporating a Texas Instrument Pressure Gage Model #145. The hydrogen was purified with a Serfass Model CH-A Hydrogen

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Purifier manufactured by the Milton Roy Company.

RESULTS AND DISCUSSION

We recently reported destruction of up to 93% of the ion radicals present on a sample of Pt black/Ce–Y zeolite/aromatic hydrocarbon when the sample was exposed at room temperature to hydrogen for 18-hr periods (*1*). We proposed that hydrogen migrated from the platinum surface as an atomic-like species and reacted with ion radicals adsorbed on the zeolite surface according to the equation:

$$H\cdot + A^{\cdot +} \rightarrow AH^{+}. \qquad (1)$$

In that study the high hydrocarbon loading of the zeolite completely saturated the surface with ion radicals (4×10^{19}/g). At this concentration ion radicals must be in close contact with neighboring ion radicals which allows the possibility of hydrogen transport through a film of adsorbed hydrocarbon.

To eliminate this possibility and to obtain information about the nature of the adsorbed ion radicals from the ESR hyperfine splitting, a 4% Pt black/Ce–Y zeolite sample was prepared and loaded with 4×10^{17} ion radicals/g. It has been shown previously that all the perylene molecules adsorbed form ion radicals (*5*). At this perylene-loading, molecules are at least 100 Å apart on the surface and cannot provide a continuous phase. This eliminates the possibility of transport of either electrons or dissociated hydrogen through an organic phase. Therefore, destruction of these ion radicals by exposure to hydrogen could be accomplished only by hydrogen migration across the zeolite surface. Figure 1a shows the spectrum obtained from this sample. The hyperfine splitting is clearly observable and is interpreted as that of the positive ion radical of perylene (*6*). The fact that it is observable at all indicates that the radicals are indeed far apart so that line broadening via dipole–dipole interaction is not important. This hyperfine splitting persists during the course of the experiment and at the end of 140 min it is still visible and appears unchanged (Fig. 1b).

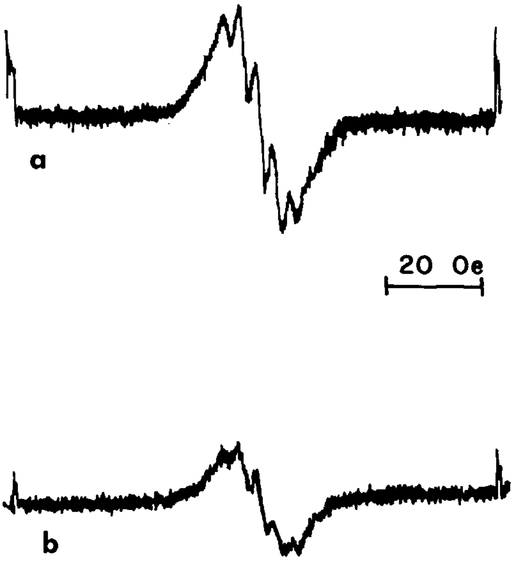

FIG. 1. Room temperature ESR spectrum of perylene positive ion radicals on 4% Pt black/CeY zeolite: (a) before addition of hydrogen; (b) 140 min after hydrogen addition.

The absence of dipolar broadening during the course of the experiment is consistent with the concept of migration of active hydrogen across the zeolite surface to sites where adsorbed perylene radicals exist. These radicals would be expected to be quite immobile at room temperature due to the strong electrostatic field between the positively charged ion and the negatively charged site on the zeolite (*7*).

Figure 2 shows the decrease of the ESR signal intensity as a function of time for the sample containing 4×10^{17} radicals/g. After 140 min, the signal intensity has been reduced to one-half its original value. Examples of the decay behavior in the absence of platinum are given in ref. (1). Typically, in the absence of Pt black the decay of the ESR signal was 10% or less than that observed when Pt black was present.

One other conclusion can be drawn from the fact that the hyperfine splitting is unchanged. This suggests that no different free radicals are generated as would be the case if hydrogen migration occurred via

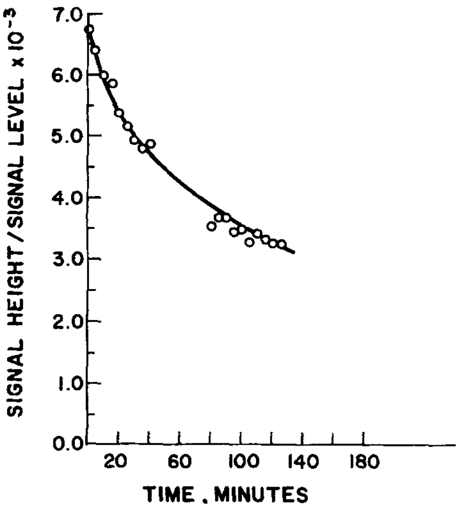

Fig. 2. Decrease of the ESR signal intensity for perylene ion radicals on 4% Pt black/CeY zeolite at room temperature in the presence of hydrogen.

simultaneous hydride ion and proton migration. The addition of a hydride ion would result in an even-alternate hydrocarbon free radical which would be expected to have different hyperfine splitting constants from the parent ion radical.

We have never observed an ESR signal which might be directly attributable to the hydrogen free radical. However, if the surface concentration of diffusing hydrogen remains very small during the spillover process, we would not expect to see such a signal due to lack of sensitivity.

When sample preparations identical to those placed in the ESR tube were placed in the gas adsorption system, extremely large hydrogen uptakes were observed. The measured uptakes were from two to three orders of magnitude larger than those necessary to completely destroy the ion radicals, and were from 7 to 35 times greater than expected for complete hydrogenation of all double bonds in the perylene molecule. These data are shown in Table 1.

In the absence of perylene, the hydrogen uptake is quite small and is due to adsorption on the platinum black only. Carbon tetrachloride does not participate in the spillover process. A blank was run in which pure CCl_4 was added and removed by our outgassing procedure. No measurable hydrogen uptake was observed. It should be emphasized that the total hydrogen uptake quantities listed in Table 1, column 2, are vastly greater than the sum of two numbers: the amount of hydrogen adsorbed on the Pt black plus the amount of hydrogen which would be consumed should every perylene molecule have its ten double bonds hydrogenated. Although we do not know if complete hydrogenation occurs, this assumption provides a maximum estimate of the hydrogen uptake attributable directly to the Pt black and the perylene. It is clear, therefore, that the adsorbed perylene functions very effectively as a bridge between the platinum and zeolite particles. No hydrogen is transferred to the zeolite in a Pt black/Ce-Y sieve mixture in the absence of perylene, yet large quantities of hydrogen migrate onto the zeolite if perylene is preadsorbed. It is also apparent that other sinks on the zeolite capable of reacting with dissociated hydrogen must exist in addition to the ion radicals. This will be discussed later in the paper.

TABLE 1

Total Hydrogen Spillover after 18 hr for Various Concentrations of Perylene on 4% Platinum Black Cerium-Y

Perylene concentration, μmoles/gram	Spillover μmoles H_2/gram	Amount $H\cdot$/perylene
0	22.7	—
0.4	138	690
1.3	233	358
2.0	157	157
4.0	646	323
8.0	609	152

Our system consists of Pt particles with an average diameter of 150 Å mixed with zeolite crystallites having an average diameter of 1450 Å. With a 5% Pt loading there is almost a 1:1 ratio between Pt and zeolite particles. The perylene is assumed to be evenly distributed on the zeolite and every contact between a perylene molecule and a Pt particle is presumed to form a bridge.

If, as our data indicate, hydrogen is transferred from the platinum and then diffuses across the zeolite, we would expect the rate of hydrogen uptake to fit a simple diffusion model. Our model consists of the following sequence of steps: (1) rapid adsorption and equilibration of hydrogen on the Pt surface; (2) transfer of dissociated hydrogen from the Pt surface through the perylene bridge onto the zeolite surface; and (3) diffusion across the zeolite to the chemical sinks where the hydrogen reacts. By making the excellent assumption that the hydrogen concentration on the Pt surface remains constant, we can use the solution for Fick's Law for diffusion away from a source of constant concentration and finite size. For small values of time, a plot of hydrogen uptake versus time to the one-half power should be linear. This linear relationship is obtained from our data and is shown in Fig. 3.

Our system may be described as radial diffusion from a disk source of radius a whose concentration is constant at C_0. The solution for Fick's Law,

$$\partial C/\partial t = D/r(\partial/\partial r)[r(\partial C/\partial r)]$$

with the boundary condition $C = C_0$, $r = a$, and $t > 0$ and the initial condition $C = 0$, $r > a$, and $t = 0$ is $C = \sqrt{(a/r)}\ C_0$ erfc $(r\text{-}a/\sqrt{4\ Dt})$ for small values of t (*8*). Here C is the surface concentration at time t at a distance r from the center of the source and D is the diffusion coefficient. The total amount of hydrogen diffused, M, will be:

$$M = \int_0^t [D\partial C/\partial r|_{r=a} 2\pi a]dt$$

which is the hydrogen flux at $r = a$ integrated with respect to time. The solution of this equation is $M = 2\sqrt{\pi}\ a\ C_0\ \sqrt{Dt}$ for small values of t.

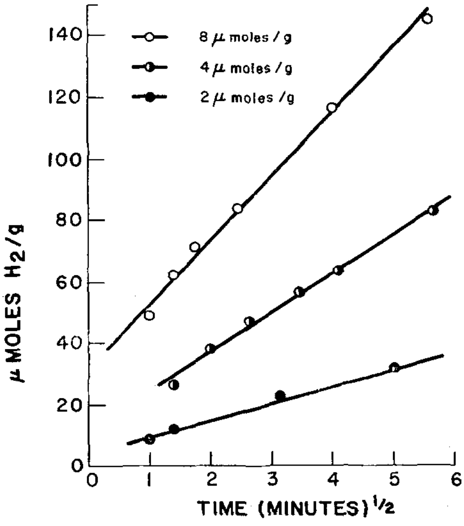

FIG. 3. The hydrogen uptake of 4% Pt black/CeY at room temperature for perylene loading of 8, 4, and 2 μmole/g.

At 300 Torr the value of C_0 on a Pt surface is 1.1×10^{-3} μmole H_2/cm^2. (*9*). We have chosen $a = 4$ Å, the approximate radius of a perylene molecule. The largest slope of Fig. 3 has a value of 21 μmole H_2/g min$^{1/2}$. Assuming each Pt particle forms one bridge with a perylene molecule and therefore acts as a source, the slope becomes 19×10^{-15} μmole H_2/Pt particle min$^{1/2}$ and the calculated diffusion coefficient is 3×10^{-10} cm^2/sec.

Mestdagh *et al.* have applied NMR techniques to measure the proton mobility in decationated Y zeolites (*10*). Their calculated diffusion coefficient at 298°K is 7×10^{-16} cm^2/sec for protons in the absence of Fe^{3+} impurities. This value should be applicable to our specially prepared Fe-free zeolite. If hydrogen were diffusing as a proton with the electron transported through the zeolite, the overall hydrogen transport rate would be limited by the slower of the two steps, either proton migration or electron conduction. We see that the value of the proton diffusion coefficient is over 5 orders of magnitude smaller than required to account for our measured spillover rates. This is further support of our belief that hydrogen migrates as an atomic-like species.

Furthermore, if the perylene molecules contacting both Pt particles and zeolite crystallites are indeed behaving as bridges, we would predict a direct proportionality between either the Pt loading or the perylene concentration and the initial rate of uptake. The appropriate limits of perylene concentration and Pt loading must be observed, however. The maximum perylene adsorption on our Ce–Y sieve is 4.4×10^{19}

molecules/g (*5*). The maximum perylene concentration used in this work was 4.8 × 10^{18} molecules/g, so we are far from the point of saturation. With our Pt particle/zeolite crystallite ratio of approximately 1, our Pt loadings are far below those which would provide so many Pt particles that not every one could contact a zeolite crystallite. Therefore, statistically, we are in a regime where doubling the perylene concentration should double the number of bridges and hence double the initial rate. A similar effect would be expected for variations in the Pt loading. This is clearly verified by Fig. 3. The slopes of these plots contain a diffusivity constant which relates directly to the number of bridges present. As the perylene concentration is varied by a ratio of 1:2:4, the initial rates vary in a ratio of 1:2.2:3.7. This shows excellent agreement and provides quantitative support of the bridging role of perylene. The proportionality between perylene concentration and rate also provides further evidence that CCl_4 does not participate in the spillover process.

It is evident that rates of spillover are enhanced by increasing platinum concentrations. In Fig. 4 we show hydrogen uptakes versus time for four different platinum loadings at constant perylene concentration. When the curves representing 1, 3, and 5% platinum are plotted versus time to the one-half power, the slopes are in the ratio 1:1.3:3.7, as compared to the loading ratio of 1:3:5. Table 2 shows the total uptake of hydrogen after 18 hr; even after this time, a dependence on Pt loading is still evident.

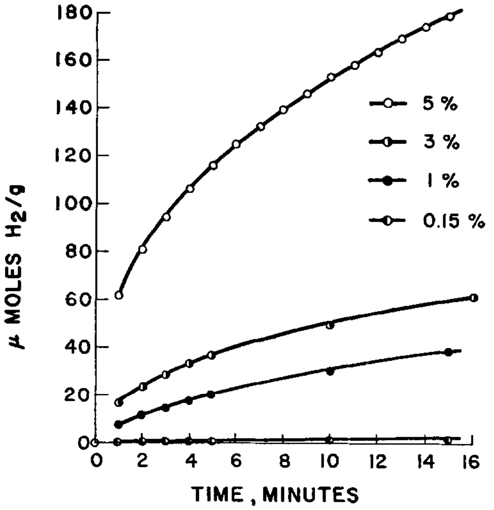

FIG. 4. The hydrogen uptake of samples of CeY zeolite for four platinum loadings (5, 3, 1 and 0.15%) at room temperature and a constant perylene loading of 8 μmoles/g.

TABLE 2

EFFECT OF PLATINUM BLACK CONCENTRATION ON TOTAL SPILLOVER (~18 HR) AT A CONSTANT PERYLENE CONCENTRATION OF 8 μMOLES/G

Catalyst	Spillover (μmoles H_2/g)
5% Pt Black/CeY	785
3% Pt Black/CeY	641
1% Pt Black/CeY	352
0.15% Pt Black/CeY	76

We may speculate at this point about the role played by the perylene bridge. During the spillover process, adsorbed hydrogen, H_{ad}, must leave the Pt surface and move to the zeolite surface. For a molecular desorption process, the activation energy of adsorption, E'_m, is the sum of the activation energy of adsorption, E, and the heat of adsorption, q. Should atomic desorption occur after adsorption of a diatomic molecule, the activation energy of desorption, E'_{at}, is one-half the sum of the heat of adsorption and the heat of dissociation, E_D. This may be seen in the plot of potential energy in Fig. 5, which represents thermodynamic states of hydrogen with regard to a Pt surface. For the desorption of an H atom, $E'_{at} = \frac{1}{2}(q + E_D)$, which has a minimum value of 52 kcal/g atom H if the heat of adsorption is assigned a value of zero. The desorption of H atoms would not be expected at room temperature. This has been our observation experimentally; in mixtures of Pt and zeolite excluding perylene, no hydrogen migration to the zeolite surface is detected although the Pt surface is covered by activated, dissociated hydrogen.

The perylene must provide an alternate

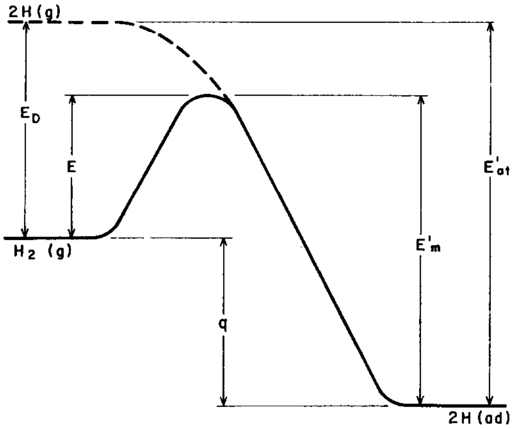

FIG. 5. Change of potential energy during absorption and desorption.

path for the transport of an atomic-like hydrogen species other than that of a gaseous hydrogen atom. This path would have a greatly reduced activation energy for removal of hydrogen from the surface, thereby allowing copious quantities of hydrogen to be transported at room temperature. There is evidence that perylene interacts readily with the hydrogen adsorbed on platinum to form a partially hydrogenated polyaromatic species (*11*). In addition, this bridging perylene species is also in contact with the zeolite surface. The presence of the hydrogen sinks, particularly any adsorbed oxygen species, would provide a driving force to extract hydrogen from the perylene complex and allow it to migrate across the zeolite surface. At this time one cannot say whether the hydrogen is extracted from the Pt surface as an atom, or is removed initially as a proton which later pulls an electron from the bulk Pt metal. We can say, however, that the hydrogen species which migrates across the zeolite surface is atomic-like since both hydrogenation and the recombination of unpaired electrons occur within the free radicals.

The question concerning the nature of the sink for hydrogen has not been considered in the past and is indeed a difficult one to answer. In the air or oxygen-activated cerium-exchanged zeolite, the cerium exists mainly in the 4^+ oxidation state (*5*). Activations of cerium-exchanged zeolites for 2 hr in air at 500°C results in a reduction in magnetic susceptibility by 80% which has been interpreted as indicating conversion from C^{3+} to Ce^{4+} (*5*). The number of Ce^{4+} ions in the zeolite corresponds closely to the maximum spillover observed, *viz.* 4.6×10^{20} Ce^{4+}/g vs 9.4×10^{20} H·/g. In addition to the ion radicals, the sink for hydrogen may be the reduction of cerium 4^+ ions according to the equation:

$$Ce^{4+} + H\cdot \rightarrow Ce^{3+} + H^+. \qquad (2)$$

There is the possibility of a third sink for hydrogen. A sample of freshly activated Ce–Y zeolite was mixed with platinum black by gently rolling the components in a vial. Portions of the sample were reactivated in air, oxygen, or helium for 2 hr at 500°, and the hydrogen uptake measured in the presence of 8 μmoles perylene/g. The uptakes are shown in Fig. 6 as a function of time. It is clear that activation in the presence of oxygen is necessary to obtain high initial rates of spillover. The fact that very little spillover occurred on the helium-activated sample (38 μmoles/g after 18 hr), even though the sample had previously been activated in oxygen where conversion of Ce^{3+} to Ce^{4+} should be extensive, suggests to us that an adsorbed oxygen species may act as a sink. The oxygen uptake of the Ce–Y zeolite at 500° and 400 Torr

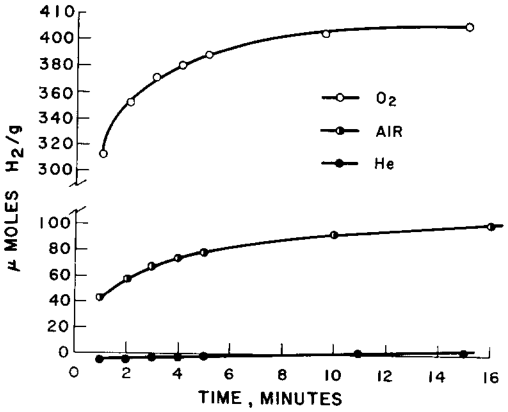

FIG. 6. The hydrogen uptake of 4% Pt black/CeY zeolite at room temperature and constant perylene loading (8 μmole/g) after activation for 2 hr at 500° in oxygen, air or helium.

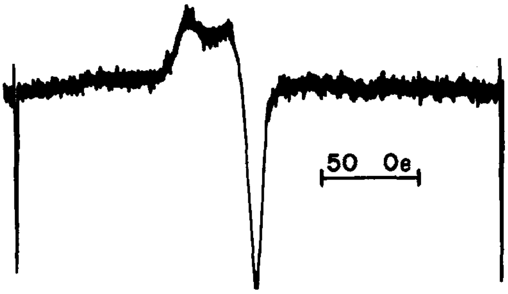

FIG. 7. The room temperature ESR spectrum of the species formed during activation of CeY zeolite at 500° for 16 hr in air.

oxygen under static conditions was 360 μmole/g. This is sufficient oxygen to account for the hydrogen uptakes observed assuming the final surface species to be hydroxyl groups or adsorbed water. However, this picture is complicated by the possibility that Ce^{4+} may revert to Ce^{3+} as oxygen desorbs during the helium activation, thereby removing Ce^{4+} sinks along with sinks due to adsorbed oxygen.

The adsorbed oxygen species may be in part O_2^-. It is reasonable that the conversion from Ce^{3+} to Ce^{4+} during activation can be represented by:

$$Ce^{3+} + O_2 \rightarrow Ce^{4+} + O_2^-. \quad (3)$$

We have observed an ESR signal (Fig. 7) from Ce–Y zeolite which can be ascribed to O_2^-. The signal is characterized by two g values, $g_{\parallel}$ and $g_{\perp}$ (2.0280 and 2.0138, respectively). An axially symmetric g value, such as appears here, can only arise when O_2^- is bonded linearly to the surface in a peroxy type linkage, e.g., $S\text{–}O\text{–}O^-$ where S is a surface site. The O_2^- signal is observed only after a long period of activation in oxygen or air. The signal disappears after evacuation at 400°. Upon reexposure of the sample to oxygen at room temperature, the signal reappears and the intensity is proportional to the oxygen pressure. We have estimated by spin counting (*5*) that the signal intensity corresponds to only 1 μmole/ of O_2^- even though 360 μmoles/g of oxygen are adsorbed. Since dipolar broadening does not result when excess oxygen is adsorbed at liquid nitrogen temperatures, it is possible that this signal arises from O_2^- adsorbed in the sodalite cages of the zeolite where accessibility to additional oxygen is limited. It appears that adsorbed oxygen, or a site closely associated with it, may be the ultimate sink for hydrogen.

CONCLUSION

We have combined ESR techniques with gas adsorption measurements to provide a comprehensive picture of hydrogen spillover in a mixture of Pt black, Ce–Y zeolite, and perylene. This system represents one of the clearest examples of hydrogen spillover and in addition provides the first insight into the nature of the migrating hydrogen species. For the first time, the rate of hydrogen spillover has been shown to be quantitatively dependent upon the number of bridging species.

The adsorbed perylene molecules not only provide a surface probe sensitive to the surface diffusion of hydrogen, but create many bridges between Pt and zeolite particles. Each bridge has been shown to allow hundreds, and possibly thousands, of hydrogen atoms to pass through to the zeolite surface. Once on the surface, the hydrogen diffuses as an atomic-like species which is most easily represented as H·. This hydrogen reacts with large quantities of chemical sinks which occur in the zeolite as a result of an activation process in oxygen. Although ESR results have indicated the sinks may be adsorbed oxygen species, the exact nature of these sinks still remains unclear. Further work is needed, not only to clearly identify these sinks, but also to provide a better understanding of the physical nature of hydrogen spillover on an atomic scale.

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