Binding and Exchange Reactions of Hydrogen Isotopes on Surfaces of Dispersed Pt Nanoparticles

Samuel L. Leung, David Hibbitts, Mónica García-Diéguez, and Enrique Iglesia*

1. INTRODUCTION

Isotopic tracer experiments and the analysis of kinetic effects of isotopic substitution are essential tools in discerning among plausible mechanisms of chemical transformations in surface catalysis. These methods are often used to assess the identity, reversibility, and kinetic relevance of elementary steps without disturbing the nature of reactants and products or the chemical steady state, thus providing direct mechanistic details, albeit often in difficult-to-interpret forms. The isotopic identity of atoms can affect the chemical reactivity of the bonds being cleaved or formed; it can also change the thermodynamic properties of molecules and the equilibrium constants for their chemical interconversions. The ratio of reaction rates or rate constants for a molecule with the most abundant isotope relative to those of its isotopologues is denoted as a kinetic isotope effect (KIE), while the corresponding ratio in their equilibrium constants is known as a thermodynamic isotope effect (TIE). These effects arise from the different mass of each isotopologue and the effects of the isotopic atom on the vibrational frequency in the bonds that contain them in reactants, products, and transition states. As a result, these methods can be used to assess the involvement of specific bonds, especially for hydrogen and deuterium atoms, in kinetically relevant and quasi-equilibrated steps within a sequence of elementary steps, as shown previously for many catalytic reactions.

Isotopic labels can be used to “trace” the fate of atoms and the molecules that contain them through reaction networks.
thus probing the reversibility of steps that form or cleave chemical bonds that include the isotope;2,19,20 these methods are broadly used in surface catalysis.6,7,21–24 

H2–D2 isotopic exchange, in particular, is often used to assess the reversibility of H2 dissociation steps on surfaces in catalytic hydrogenation–dehydrogenation events

\[
\begin{align*}
H_2 + 2\gamma &\leftrightarrow 2H\gamma \\
D_2 + 2\gamma &\leftrightarrow 2D\gamma \\
HD + 2\gamma &\leftrightarrow H\gamma + D\gamma
\end{align*}
\]

These experiments and interpretations, however, implicitly assume that isotopic scrambling events occur only via the dissociative adsorption and recombinative desorption reactions represented in eqs 1–3; such pathways are denoted here as the “recombinative desorption” mechanism. Isotopic exchange between H2 and D2 and para–ortho hydrogen interconversion reactions were previously examined on Pt wires under high-vacuum conditions; these studies concluded that single-site exchange events between H2 and bound D* adatoms (and D2 and H* adatoms) occur, possibly without requiring surface-mediated dissociation of H–H bonds in H2 even below 200 K.25 Similar conclusions were reached by Christmann et al. using H2 and D2 thermal desorption studies;26 such pathways have also been proposed on other metals (Ni, Cu, Ag, Au).27–32 These studies, however, did not provide unequivocal kinetic evidence for such mechanisms at the pressures and temperatures relevant for catalytic turnovers; as a result, such conclusions are seldom cited in later studies that exploit such methods to assess the reversibility of H2 dissociation events (eqs 1–3) during catalysis. These previous H2–D2 exchange studies also did not place the proposed exchange routes firmly within the context of the thermodynamics of H2 and D2 chemisorption on surfaces, which have been treated independently in later studies (e.g., Pt33–39).

This study addresses the kinetics of H2–D2 isotopic exchange on Pt-based catalysts and the magnitude of H2/D2 TIEs under conditions of catalytic relevance. H2 and D2 chemisorption isotherms obtained at 523–673 K (10−4 to 103 kPa H2 or D2; 0.1–0.8 monolayer coverages) are nearly identical at each temperature, reflecting TIE values near unity. These TIE values depend very weakly on temperature, consistent with dissociative chemisorption enthalpies for H2 and D2 on Pt surfaces that differ by only 4.2 ± 1.2 kJ mol−1; these enthalpies can be used to calculate equilibrium coverages of H* and D* for H2–D2 mixtures at other temperatures.

H2–D2 exchange rates on Pt catalysts at 383 K increase monotonically with H2 and D2 pressure (5–800 kPa H2, 5–800 kPa D2). Exchange rates are also nearly identical when H2 and D2 pressures are switched, in contrast with the rate differences expected from TIE values at 383 K (0.6 ± 0.2). These kinetic data are inconsistent with the recombinative desorption mechanism (eqs 1–3) as the predominant route for H2–D2 isotopic exchange. An alternate route, in which H2 adsorbs non-competitively with an equilibrated H*/D* adlayer and reacts with D* (and D2 reacts with H*),25,27–32 is, however, consistent with all experimental and theoretical evidence. These reactions (H2–D* and D2–H*) provide an alternate reaction pathway that leads to H*/D* surface compositions set by the kinetics of exchange events instead of the thermodynamics of H2 and D2 dissociative adsorption. H2–D* and D2–H* reactions are shown to exhibit KIE values (defined as the ratio of rate constants for H2–D* and D2–H* reactions) near unity (1.1 ± 0.3). Such routes, denoted here as “non-competitive adsorption” pathways, are consistent with the absence of a maximum in exchange rate near equimolar H2–D2 compositions. These exchange reactions, which resemble in the functional forms of the rate equation those for Eley–Rideal kinetics,51 remain the dominant pathway at all temperatures below 700 K (5–40 kPa, total H2/D2 pressure).

The kinetic behavior of H2–D2 exchange cannot distinguish various structurally distinct H2–D* and D2–H* reaction mechanisms and the interactions involved at the transition state. Density functional theory (DFT) calculations on flat Pt(111) surfaces and 201-atom Pt nanoparticles show that these exchange events are mediated by dissociation of H2 or D2 on Pt surfaces at sites that form via the displacement of single H* and D* adatoms to alternate binding modes within the equilibrated mobile H*/D* adlayers prevalent at these temperatures (383–700 K); such pathways do not require the desorption of an H* or a D* atom for exchange turnovers to occur. H2–D2 isotopic exchange thus occurs via pathways that circumvent the recombinative desorption of H* and D* (the reverse of eqs 1–3). Consequently, exchange rates cannot be used to unequivocally demonstrate reversibility of H2 adsorption (eqs 1–3) under conditions of catalytic hydrogenation/dehydrogenation reactions.

2. METHODS

2.1. Catalyst Synthesis Methods. Pt nanoparticles dispersed on SiO2 (0.2% wt, Pt/SiO2-A) were prepared using strong electrostatic adsorption methods28 that exploit interactions between SiO2 surfaces that are negatively charged at the prevalent solution pH (11.4) and aqueous cationic Pt precursors ([Pt(NH3)4(NO3)2]; 99.99% metals basis, Alfa Aesar) to form well-dispersed strongly bound precursors. SiO2 (Davisl, grade 62, Sigma-Aldrich) was treated before Pt deposition in flowing air (0.83 cm3 g−1 s−1; zero grade, Praxair) while ramping from ambient temperature to 1073 K (0.083 K s−1), holding for 5 h, and cooling to ambient temperature. [Pt(NH3)4](NO3)2 (0.0060 g) and SiO2 (1.5 g) were then added to 25 cm3 of a 0.4 M NH4OH solution, prepared by diluting a 25% solution NH4OH (Sigma-Aldrich) in deionized (DI) water (>18.0 MΩ cm resistivity) and stirring for 2 h. The solids were filtered and rinsed three times with DI water (100 cm3 g−1) and treated overnight in ambient stagnant air at 368 K. Samples were then treated in flowing air (1.67 cm3 g−1 s−1; zero grade, Praxair) while heating from ambient temperature to 873 K (0.083 K s−1) and holding for 3 h before again cooling to ambient temperature. This was followed by treatment in flowing H2 (1.67 cm3 g−1 s−1; 99.999% UHP; Praxair) while ramping to 1073 K (0.083 K s−1) and holding for 2 h. After cooling, the sample was exposed to flowing 2% mol O2 (balance He) (1.67 cm3 g−1 s−1; certified grade, Praxair) for 0.5 h at ambient temperature. This O2 treatment is intended to passivate Pt nanoparticles surface, thus avoiding exothermic oxidation processes upon contact with ambient air. A second sample of Pt/SiO2 (0.2% wt, Pt/SiO2-B) was prepared using similar steps but treated in flowing air and H2 at 623 K instead of 873 K to avoid additional structural changes caused by exposure to higher temperatures.

Pt nanoparticles dispersed on γ-Al2O3 (1% wt, Pt/γ-Al2O3-A) were prepared by incipient wetness impregnation. γ-Al2O3 (Sasol, CATALOX SBA 200) was treated before Pt deposition in flowing air (0.83 cm3 g−1 s−1; zero grade, Praxair) while ramping to 1073 K (0.083 K s−1) and holding for 5 h. An
aqueous solution of H₄PtCl₆ (2.4% wt in H₂O) was prepared by diluting an aqueous solution of H₂PtCl₆ (8% wt in H₂O, Sigma-Aldrich) in DI H₂O (>18.0 MΩ cm resistivity) and added dropwise to γ-Al₂O₃ (0.86 cm³ g⁻¹ γ-Al₂O₃). The sample was treated in ambient air at 368 K overnight and then in flowing air (1.67 cm³ g⁻¹ s⁻¹; zero grade; Praxair) by heating from ambient temperature to 773 K (at 0.033 K s⁻¹) and holding for 3 h before cooling to ambient temperature. This procedure was followed by treatment in flowing H₂ (1.67 cm³ g⁻¹ s⁻¹; 99.999% UHP; Praxair) while heating to 1073 K (at 0.083 K s⁻¹) and holding for 2 h. After cooling, the sample was treated in a 2% O₂/He stream (certified grade; Praxair) for 0.5 h at ambient temperature in order to passivate the surfaces of the Pt nanoparticles.

Pt/SiO₂ (5% wt, Pt/SiO₂-C) and Pt/γ-Al₂O₃ (1.6% wt, Pt/γ-Al₂O₃-B) samples were also prepared and used in H₂ and D₂ uptake experiments to measure TIE values. Pt/γ-Al₂O₃-B was prepared as reported previously.33 Pt/SiO₂-C was prepared by incipient wetness impregnation of SiO₂ (Cabosil, HS-5, 310 m² g⁻¹) with an aqueous solution of Pt(NH₃)₄(NO₃)₂ (Alfa Aesar, CAS 20634-12-2). This sample was treated in flowing dry air (99.99%, 0.8 cm³ g⁻¹ s⁻¹, Praxair) at 673 K (0.033 K s⁻¹) for 3 h and then treated in flowing 9% H₂/He (Praxair, 1.67 cm³ g⁻¹ s⁻¹) by heating from ambient temperature to 773 K at 0.033 K s⁻¹ and holding for 3 h. It was then passivated at ambient temperature by exposure to flowing 0.5% O₂/He (Praxair, certified grade, 0.05 cm³ g⁻¹ s⁻¹) for 1 h before contact with ambient air.

Pt black (Strem Chemicals, a 22.7 m² g⁻¹ nominal surface area) was used as received and treated before H₂−D₂ kinetic experiments, as described below.

2.2. Measurement of H₂ and D₂ Chemisorption Isotherms. The dispersion values, defined as the ratio of the number of exposed Pt sites to the total number of Pt atoms, for Pt/SiO₂-A, Pt/SiO₂-B, and Pt/γ-Al₂O₃-A samples were measured from H₂ chemisorption uptakes. Samples (ca. 1 g) were treated in flowing H₂ (99.999% UHP; Praxair; 0.33 cm³ g⁻¹ s⁻¹) at 673 K (0.083 K s⁻¹) while heating to 1073 K (at 0.1 K s⁻¹) and then evacuated (<10⁻⁵ Pa) at this temperature for 1 h. The sample was then cooled in vacuum to 373 K. H₂ chemisorption uptakes were measured at 1−40 kPa H₂ and 373 K. Saturation uptakes were determined by linear extrapolation of the uptakes to zero H₂ pressure. Nanoparticle diameters were calculated using the following relations:41

\[ d = \frac{f_{\text{shape}} N_M}{2N_H_2} \frac{v_a}{a_m} \theta_{\text{sat}} \]  

(4)

\[ \theta_{\text{sat}} = H/Pt_a = 1 + \alpha(d^{-1}) + \beta(d^{-2}) \]  

(5)

Here, \( d \) is the diameter of the particle; \( f_{\text{shape}} \) is a shape factor (6 for a hemispherical particle); \( N_M \) is the total number of metal atoms; \( N_H_2 \) is the number of H₂ molecules dissociated on the surface; \( v_a \) and \( a_m \) are the volume and surface area of a Pt atom (calculated from the bulk density of Pt, 21.45 g cm⁻³); 42 and \( \alpha \) (0.0364) and \( \beta \) (0.735) are empirical parameters specific for Pt.9 Pt denotes atoms on the metal surface. This system of equations (eqs 4 and 5) can be solved iteratively to obtain the particle diameter (\( d \)) and saturation coverage (\( \theta_{\text{sat}} \)) in a manner that corrects for supra-stoichiometric H⁺ coverages that arise from the binding of multiple H atoms on corner and edge sites on small metal nanoparticles.41

H₂ and D₂ chemisorption uptakes (523−673 K at 0.1−30 kPa H₂ or D₂) were also measured on Pt/SiO₂-C and Pt/γ-Al₂O₃-B samples to determine TIE values for dihydrogen dissociative adsorption. Samples (ca. 1 g) were treated at 723 K in flowing H₂ (1.33 cm³ g⁻¹ s⁻¹; UHP grade, Praxair; a 0.083 K s⁻¹ heating rate) for 1 h and then evacuated for 2 h. After evacuation, samples were brought to the target chemisorption temperature, and H₂ (or D₂) uptakes were measured by increasing the H₂ (or D₂) pressure from 0.1 to 30 kPa (H₂ or Praxair, UHP; D₂, Spectra Gases Inc., UHP). The apparent cell volume was determined at each temperature using He as a non-adsorbing inert gas.

2.3. Measurement of Isotopic Exchange Rates. Isotopic exchange rates were measured on samples (0.0005−0.0500 g, <100 μm aggregate diameter) held on a quartz frit within a U-shaped quartz tube (6.35 mm O.D.; 4 mm I.D.). H₂ (99.999% UHP; Praxair), D₂ (99.8% isotopic purity, Research Grade; Praxair), and N₂ (99.998%, Praxair) streams were treated using purifiers (VICI Metronics) designed to remove residual H₂O and O₂. Molar flow rates were controlled using electronic mass flow controllers (Parker Porter 200 series). Samples were treated in flowing H₂ (100 cm³ g⁻¹ s⁻¹) while heating from ambient temperature to 873 K (at 0.083 K s⁻¹) for Pt/SiO₂-A, Pt/γ-Al₂O₃-A, and Pt black samples and to 623 K for Pt/SiO₂-B samples and then holding for 2 h before isotopic exchange rate measurements.

The inlet and outlet streams were speciated using mass spectrometry (Leybold Inficon Transpector, TSP TH200). H₂−D₂ exchange rates were determined by correcting measured rates (\( r_n \)) for approach to isotopic equilibrium (\( \eta \)) to give forward rates (\( r_f \)) using

\[ r_n = r_f (1 - \eta) \]  

(6)

The approach to equilibrium (\( \eta \)) for H₂−D₂ exchange

\[ H_2 + D_2 \rightarrow 2HD \]  

(7)

is defined as

\[ \eta = \frac{K_{HD}}{(H_2)(D_2)} \]  

(8)

(\( i \)) denotes the pressure of species \( i \) (in kPa). \( K_{HD} \) is the equilibrium constant for H₂−D₂ exchange; it equals 4 at all temperatures, corresponding to the binomial isotopologue distribution.43 The thin catalyst beds used in these experiments exhibit hydrodynamics that resemble well-mixed systems; thus, exit concentrations were used in eq 8. The absence of diffusional corruptions of measured exchange rates was confirmed by similar measured exchange rates as the size of the catalyst aggregates varied (smaller particles, <50 μm aggregate diameter, were obtained by grinding catalyst samples into fine powders; SI-1).

2.4. Computational Methods. Periodic plane wave DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)44,45 as implemented in the computational catalysis interface.46 Plane waves were constructed using projector augmented waves47−49 with an energy cutoff of 396 eV. (This value errs on the side of greater accuracy and was chosen to facilitate follow-up studies that include H₂−D₂ exchange in the presence of H₂O.) The revised Perdew−Burke−Ernzerhof (RPBE) form of the generalized gradient approximation (GGA) was used to describe exchange and correlation energies.50,51 Wave functions were converged
until the electronic energies varied by less than $10^{-6}$ eV. Forces on all atoms were determined using a fast Fourier transform grid with a cutoff equal to twice the plane wave cutoff; the geometries of all structures were optimized until the forces on all atoms were smaller than 0.05 eV nm$^{-1}$.

H$_2$ molecules in the gas phase were modeled by placing them within a $1.8 \times 1.8 \times 1.8$ nm vacuum unit cell. Pt(111) surfaces were modeled as $3 \times 3$, $4 \times 4$, and $6 \times 6$ closed-packed periodic lattices with four layers orthogonal to the surface and 1 nm of vacuum separating slabs; the bottom two layers were fixed at their bulk positions (an fcc crystal with unit cell parameter of 0.39239 nm), and the top two layers were relaxed. Sampling of the Brillouin zone depended on the size of the metal surface. For $4 \times 4$ Pt(111) surfaces, a $3 \times 3 \times 1$ Monkhorst–Pack sampling of the first Brillouin zone (k-point mesh) was used during geometric convergence iterations; after convergence, a single-point calculation with a $6 \times 6 \times 1$ k-point mesh was performed to determine electronic energies. These k-point meshes were adjusted to consistently capture long-range interactions for $3 \times 3 \times 3$ Pt(111) surfaces to $4 \times 4 \times 1$ and $8 \times 8 \times 1$ for the geometric convergence and single-point calculation, respectively. For $6 \times 6$ Pt(111) surfaces, the meshes were $2 \times 2 \times 1$ and $4 \times 4 \times 1$. Symmetric cubo-octahedral Pt nanoparticles (Pt$_{201}$, 201 atoms, a 1.4 nm diameter) with 1.4 nm of vacuum between metal atoms were also examined as model systems, as described in detail in previous reports. The Brillouin zone was sampled only at the Γ-point for nanoparticle model calculations.

Vibrational frequencies were calculated for bound species and transition states using a fixed displacement method (two displacements per mode), in which all metal atoms were fixed and all H atoms (ranging from 9 to 38 total H atoms) were allowed to vibrate for Pt(111) calculations. For Pt$_{201}$ nanoparticle calculations, only the reacting H$_2$ and H* on the active (111) terrace were allowed to vibrate (19–33 total H atoms). These frequency calculations were used, together with statistical mechanic formalisms and harmonic oscillator models, to estimate vibrational zero-point energies, enthalpies, entropies, and Gibbs free energies. For gaseous H$_2$ molecules, the translational and rotational enthalpies and free energies were also computed instead of using experimental values.

The atomic masses of elements (i.e., using the H or D isomer) have negligible impacts on the potential energies but do impact the enthalpies and free energies of species by altering vibrational frequencies and thus zero-point vibrational energies as well as the vibrational enthalpies and free energies through statistical mechanics formalisms. For gaseous molecules, atomic masses affect the rotational and translational contributions to free energies; as a result, they influence barriers when transition-state free energies are referenced to gaseous H$_2$ (or D$_2$), as required for comparisons with experimental values in this study. Enthalpy barriers for H$_2$ or D$_2$ reactions can thus be calculated from statistical mechanics by altering atomic weights when calculating vibrational, translational, and rotational partition functions to estimate the kinetic effects of isotopes from free-energy barriers.

### 3. RESULTS AND DISCUSSION

#### 3.1. Pt Dispersions and Nanoparticle Diameters.

Fractional Pt dispersions were measured for three Pt/SiO$_2$ samples and two Pt/γ-Al$_2$O$_3$ samples; these data were used to calculate nanoparticle diameters using eqs 4 and 5 (Table 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal Pt Content (% wt)</th>
<th>Dispersions</th>
<th>Mean Nanoparticle Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO$_2$-A</td>
<td>0.2</td>
<td>0.38</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt/SiO$_2$-B</td>
<td>0.2</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Pt/SiO$_2$-C</td>
<td>5.0</td>
<td>0.32</td>
<td>3.8</td>
</tr>
<tr>
<td>Pt/γ-Al$_2$O$_3$-A</td>
<td>1.0</td>
<td>0.72</td>
<td>1.9</td>
</tr>
<tr>
<td>Pt/γ-Al$_2$O$_3$-B*</td>
<td>1.6</td>
<td>0.37</td>
<td>3.3</td>
</tr>
</tbody>
</table>

*Synthesis and characterization reported in a previous study. Calculated by assuming hemispherical particle geometries and using the bulk density of Pt (21.45 g cm$^{-3}$).

3.2. H$_2$ and D$_2$ Uptake on Pt/SiO$_2$-C and Pt/γ-Al$_2$O$_3$-B and Thermodynamic Isotope Effects. H$_2$ and D$_2$ chemisorption uptake values were measured on 5.0% wt Pt/SiO$_2$-C and 1.6% wt Pt/γ-Al$_2$O$_3$-B samples at 623 K (10$^{-3}$ to 10$^{-2}$ kPa). H$_2$ and D$_2$ uptake isotherms (Figure 1) were very similar on each sample; the uptakes (of both isotopes) differed between Pt/SiO$_2$-C and Pt/γ-Al$_2$O$_3$-B because of their different metal dispersion (Table 1). These uptake data were used to determine dissociative adsorption equilibrium constants for H$_2$ ($K_{H_2}$) and D$_2$ ($K_D$)

$$K_{H_2} = \frac{\theta_{H_2}^2}{(H_2)\theta_f^2}$$

$$K_D = \frac{\theta_{D_2}^2}{(H_2)\theta_f^2}$$

Figure 1. H$_2$ (●, ○) and D$_2$ (▲, △) adsorption isotherms on Pt/SiO$_2$-C (closed symbols) and Pt/γ-Al$_2$O$_3$-B (open symbols) at 623 K.
(0.90 ± 0.07) and Pt/γ-Al2O3-B (0.81 ± 0.10) at all H2 and D2 pressures (10^-4 to 10^1 kPa) and coverages and agree well with DFT-derived values for Pt(111) surfaces (0.68, 0.87, and 0.91 for atop, fcc, and hcp binding modes, respectively; 1 H/Pt, 623 K).57

H2 and D2 adsorption isotherms were also measured at other temperatures (523−673 K; isotherms and equilibrium constants in SI-2) on 1.6% wt. Pt/γ-Al2O3-B to determine temperature effects on TIE values. Figure 3 shows the average TIE values (523−673 K), reflecting the mean over the range of fractional coverages (0.19−0.57) in view of their weak coverage dependence (Figure 2). These values are nearly independent of temperature (Figure 3), within experimental uncertainty, and reflect the small differences in H2 and D2 adsorption enthalpies (ΔH_D2,ads - ΔH_H2,ads = -4.1 ± 1.4 kJ mol^{-1}) and entropies (ΔS_D2,ads - ΔS_H2,ads = 5.0 ± 2.0 J mol^{-1} K^{-1})

TIE = \( \frac{K_H}{K_D} \)

Equation 11 can be used to extrapolate TIE values to other temperatures and to infer the relative coverages of H* and D* (eqs 9 and 10) under the conditions of isotopic exchange, described in the following section.

3.3. Effects of H2 and D2 Pressures on Exchange Rates and Implications for the Identity and Kinetic Relevance of Elementary Steps. H2−D2 isotopic exchange turnover rates were measured at 383 K over a range of H2 and D2 pressures (5−80 kPa) on 0.2% wt. Pt/SiO2-A (3.2 nm, Table 1). The HD formation rates were below detection limits on a Pt-free SiO2 sample under these conditions. Figure 4 shows
that exchange rates increased monotonically with increasing H2 or D2 pressure (5–80 kPa; 0.0625–16 H2/D2 molar ratios). HD formation rates were nearly identical when the H2 and D2 pressures were switched (as shown by significant overlap between the open and filled symbols of a given type in Figure 4).

These kinetic trends are examined first in the context of the commonly proposed “recombinative desorption” mechanism (eqs 1–3) that such trends, in fact, contradict. HD formation events mediated by recombination of H* and D* (eq 2) depend on the H* and D* coverages set by the thermodynamics of H2 and D2 dissociative adsorption and reach maximum values at H2 and D2 pressures that lead to identical H* and D* coverages. The chemisorption uptakes reported here (Section 3.2) and in previous studies indicate that Pt surfaces are nearly saturated with H* or D* at all pressures and temperatures used in these exchange experiments [(H2) + (D2) > 10 kPa; 383 K]. H* and D* coverages can thus be described by extrapolating TIE ratios from H2/D2 chemisorption data on Pt/γ-Al2O3-B ([23–673 K; Figure 3; Section 3.2]) to 383 K, which gives a value of 0.6 ± 0.2. This TIE value (0.6, 383 K) indicates that H* and D* coverages become equal at H2/D2 molar ratios of about 1.3, a value estimated by assuming that such TIE values are set by those for desorption rates (derivation in SI-3.1). When TIE values are unity, the rate of HD formation is given by (SI-3.1)

\[ r_{\text{HD,j}} = k_\gamma \theta_i (H_2/D_2)^j ((H_2) + (D_2))^2 \]  

and HD formation rates reach a maximum at H2/D2 molar ratios of unity. Measured HD formation rates, however, increased monotonically with increasing H2 and D2 pressure (Figure 4), even at very high H2/D2 molar ratios (16). Such trends are inconsistent with the dissociation–recombination exchange routes depicted by eqs 1–3 and with the rate equation associated with such elementary steps (eq 12). These exchange rate data are also inconsistent with a two-site mechanism, in which H2 and D2 molecules adsorb and react in a concerted manner with H*–H*, H*–D*, or D*–D* pairs at surfaces; this latter mechanism would give the rate equation (derivation in SI-3.2, assuming a TIE value of unity)

\[ r_{\text{HD,fi}} = [64k_\gamma \theta_i (H_2/D_2)^j ((H_2) + (D_2))^2 \]  

\{ (H_2)^6 + (D_2)^6 + 11(H_2)^2(D_2)^4 + 11(D_2)^2(H_2)^4 \ (\gamma(H_2)^6 + (D_2)^4 + 4(H_2)^2(D_2)^2) \} \]  

\[ \div [3(H_2)^2 + (D_2)^2 - \gamma^2(3(D_2)^2 + (D_2)^2 - \gamma^2)] \]  

\[ \gamma = \sqrt{(H_2)^2 + 14(H_2)^2(D_2)^2 + (D_2)^4} \]  

Equations 13 and 14 similarly predict a maximum in HD formation rate at H2/D2 molar ratios near unity, in contradiction of the trends in Figure 4. Parity plots of measured and predicted HD formation rates (Figure S4 in SI-4) confirm that these mechanisms are inadequate to describe measured exchange rates.

An alternate exchange pathway is a single-site route in which gaseous H2 and D2 molecules react with single D* and H* adatoms to exchange their isotopes, as suggested in previous studies; these studies proposed that gaseous H2 molecules react directly with D* adatoms (or D2 with H*) via an “associative” concerted pathway. Such single-site routes may also reflect the adsorption of H* and D* at non-competitive sites and their subsequent reaction with D* and H*, as shown in the present study from DFT treatments (Section 3.6). These “non-competitive adsorption” exchange pathways are depicted as steps 1.4–1.5 in Scheme 1, together with the dissociative–recombinative reactions (steps 1.1–1.3).

**Scheme 1. Dissociative–Recombinative (1.1–1.3) and Non-Competitive Adsorption (1.4–1.5) Elementary Steps for H2–D2 Isotopic Exchange**

\[ H_2 + 2^* \xrightarrow{k_1} 2H^* \]  

\[ HD + 2^* \xrightarrow{k_2} H^* + D^* \]  

\[ D_2 + 2^* \xrightarrow{k_3} 2D^* \]  

\[ H_2 + D^* \xrightarrow{k_4} HD + H^* \]  

\[ D_2 + H^* \xrightarrow{k_5} HD + D^* \]

Here, \( k_\gamma \) is the fractional coverage of species \( i \). Equation 15 contains separate terms for H2–D* and D2–H* reactions (steps 1.4–1.5, Scheme 1) to take into account any KIEs (KIE\(_{ex}\) = \( k_\gamma/k_\delta \)) for these exchange events. The value of KIE\(_{ex}\) can be inferred here from the HD formation rates that are nearly identical when the magnitudes of the H2 and D2 pressures are switched (Figure 4, indicated by overlapping open and filled symbols of a given type). We define a parameter \( \gamma_{ij} \) as an inlet stream with H2 pressure \( i \) and D2 pressure \( j \) (in kPa). Figure 5 shows that the ratios of rates defined as

**Figure 5. Rate ratios \( \gamma_{ij} = \left( \frac{r_{H_2/D_2}^{i,j}}{r_{H_2/D_2}^{i,j}} \right) \) for reactant mixtures \( \gamma_{ij} \) (H2 pressure \( i \) and D2 pressure \( j \)). Calculated ratios are included for KIE\(_{ex}\) (\( k_\gamma/k_\delta \)) values of 0.5 (■) and 2.0 (▲) for comparison.**
\[
\chi_{ij} = \frac{r_{\text{HD}}(x_{ij})}{r_{\text{HD}}(y_{ij})}
\]  

(16)

are near unity (1.01 ± 0.05) for all \(H_2-D_2\) pressure pairs. The \(\chi_{ij}\) values were also calculated (details in SI-5) using various KIE_{ex} \((k_i/k_o)\) values (0.5–2) that led to significant deviations of \(\chi_{ij}\) values from unity (0.6–1.7; Figure 5). These experimental values of \(\chi_{ij}\) show that KIE_{ex} \((k_i/k_o)\) values are near unity (1.1 ± 0.3), in agreement with values derived later using theoretical methods (Section 3.6). These \(\chi_{ij}\) values near unity differ from those expected for \(H^*\) and \(D^*\) coverages derived from the TIE value at 383 K (0.6 ± 0.2). Such deviations suggest that the \(H_2\) and \(D_2\) dissociation reactions (steps 1.4–1.5, Scheme 1) that mediate the exchange of hydrogen and deuterium atoms occur at rates much faster than dissociation–recombination events (steps 1.1–1.3, Scheme 1). Fractional \(H^*\) \((\theta_i)\) and \(D^*\) \((\theta_o)\) coverages in this case (for a KIE_{ex} value of 1) are, as for a TIE value of unity, described by (derivation in SI-3.3)

\[
\theta_H = \frac{(H_2)}{(H_2) + (D_2)}
\]

(17)

\[
\theta_D = \frac{(D_2)}{(H_2) + (D_2)}
\]

(18)

These \(H^*/D^*\) ratios (eqs 17 and 18) are equal to the \(H_2/D_2\) ratios in the contacting gas phase.

Equations 17 and 18 can be substituted into eq 15 to give

\[
r_{\text{HD},i} = k_{-2}((H_2)(D_2)) + 2k_{i}(H_2)(D_2) = k_{-2} + 2k_{i}(H_2) + (D_2))
\]

(19)

for KIE_{ex} \((k_i/k_o)\) values of unity. This equation includes terms for dissociation–recombination reactions \((k_{-2}\frac{(H_2)(D_2)}{(H_2) + (D_2)}\), steps 1.1–1.3, Scheme 1) and non-competitive-adsorption-mediated exchange reactions \((2k_{i}\frac{(H_2)(D_2)}{(H_2) + (D_2)}\), steps 1.4–1.5, Scheme 1). Equation 19 can also be expressed in a linear form that allows the rate constants \(k_{-2}\) and \(k_{i}\) (normalized per surface site) to be regressed linearly from measured isotopic exchange rates

\[
r_{\text{HD},i}((H_2) + (D_2)) = k_{-2} + 2k_{i}(H_2) + (D_2))
\]

(20)

Figure 6 shows these rates at 383 K according to the functional form of eq 20. The value of \(k_{-2}\) \((-2.1 ± 20 \text{ s}^{-1})\) is given by the y-intercept of the data in Figure 6, while the value of \(k_{i}\) \((9.1 ± 0.2 \text{ kPa}^{-1} \text{ s}^{-1})\) is reflected in the slope (uncertainties are defined as 95% confidence intervals). The near-zero value and large uncertainty of \(k_{-2}\) show that recombinative hydrogen desorption reactions (steps 1.1–1.3 in Scheme 1) are much slower than \(H_2-D^*\) and \(D_2-H^*\) exchange routes (steps 1.4–1.5 in Scheme 1), as previously suggested by \(\chi_{ij}\) values near unity (Figure 5); consequently, such dissociative routes contribute negligibly to measured exchange rates under these reaction conditions (383 K, 5–80 kPa \(H_2\) or \(D_2\)). A sensitivity analysis of \(k_{-2}\) indicates that the rates of recombination are below the detection limit of these experiments (SI-6). A parity plot of the HD formation rates modeled by eq 20 and Scheme 1 is shown as Figure S4c in SI-4.

These data and mechanistic considerations, later probed also by theoretical treatments (Section 3.6), show that \(H_2-D_2\) exchange occurs on surfaces saturated with a mixture of \(H^*\) and \(D^*\) adatoms at relative coverages dictated by the reactions of \(H_2\) with \(D^*\) and \(D_2\) with \(H^*\) (steps 1.4–1.5, Scheme 1) with KIE values near unity; these steps occur much faster than \(H_2\) or \(D_2\) dissociation or \(H^*\)–\(H^*\), \(H^*\)–\(D^*\), and \(D^*\)–\(D^*\) recombination reactions (steps 1.1–1.3 in Scheme 1) and lead to \(H^*/D^*\) ratios that resemble \(H_2/D_2\) molar ratios in the contacting gas phase. Consequently, the specific value of the TIE for \(H_2\) and \(D_2\) dissociative adsorption does not influence \(H_2-D_2\) isotopic exchange rates.

3.4. Effects of Temperature and \(H^*/D^*\) Coverage on Isotopic Exchange Rates. \(H_2-D_2\) exchange rates were measured at temperatures between 303 and 1000 K on Pt/SiO₂-A at \(H_2\) and \(D_2\) pressures between 2 and 20 kPa. HD formation rates via recombinative desorption routes (step 1.2, Scheme 1) would depend only on the relative ratio of \(H_2\) and \(D_2\) and remain independent of total pressure at each given \(H_2/D_2\) ratio (first term in eq 19), in contrast with \(H_2-D^*\) and \(D_2-H^*\) non-competitive adsorption reactions, which would depend also on the total \(H_2\) and \(D_2\) pressure (through the second term in eq 19). As a result, lower combined \(H_2/D_2\) pressures lead to smaller relative contributions of \(H_2-D^*\) and \(D_2-H^*\) reactions (steps 1.1–1.3, Scheme 1) and its rate parameter \(k_{-2}\) thus become easier to detect at lower total pressures of \(H_2\) and \(D_2\), as shown by rearranging eq 19 as

\[
r_{\text{HD},i}((H_2) + (D_2)) = k_{-2} + 2k_{i}(H_2) + (D_2))
\]

(21)

The value of \(k_{-2}\) and its temperature dependence become measurable at sufficiently low combined \(H_2\) and \(D_2\) pressures.

Figure 7 shows \(r_{\text{HD},i}((H_2) + (D_2))\) ratios (left-hand side of eq 21) at several \(H_2\) and \(D_2\) pressures (2–20 kPa) as a function of temperature in an Arrhenius-type plot. These data deviate from linear trends at temperatures above 700 K (Figure 7b); these deviations become more evident at lower combined \(H_2/D_2\) pressures as contributions from dissociation–recombination

![Figure 6. H₂–D₂ exchange rate data at 5 (●), 10 (■, □), 20 (▲), and 40 (◇, △) kPa H₂ (open symbol) or D₂ (closed symbol) at 383 K on 0.2% wt Pt/SiO₂-Å, linearized in accordance with eq 20. The dashed line represents linear regression of the data.](https://doi.org/10.1021/acs.jpcc.1c09131)
The contributions from the non-competitive adsorption routes (2k\textsubscript{ij} eq 21) at high temperatures (>700 K) were estimated by extrapolating the data from temperatures at which \( \frac{r_{\text{HD},f}(H_2) + (D_2)}{(H_2)(D_2)} \) values (left-hand side: eq 21) became similar at all (H\textsubscript{2})+(D\textsubscript{2}) pressures (2–20 kPa, 303–600 K) (Figure 7a); such convergence indicates that these data reflect dominantly contributions from H\textsubscript{2} + D* and D\textsubscript{2} + H* pathways (steps 1.4–1.5, Scheme 1) and its rate parameter (k\textsubscript{1,2} eq 21). The k\textsubscript{1,2} values can be obtained using eq 21 by subtracting the contributions from non-competitive adsorption routes (2k\textsubscript{ij} eq 21; H\textsubscript{2} + D* and D\textsubscript{2} + H*), steps 1.4–1.5, Scheme 1) from the total exchange rates measured at high temperatures (750–1000 K, 2 kPa H\textsubscript{2}, 2 kPa D\textsubscript{2}; Figure 7b, indicated by dashed line). The temperature dependence of the k\textsubscript{1,2} values obtained using these methods of analysis gave a larger activation barrier (78 ± 11 kJ mol\textsuperscript{-1}) than for the low-temperature route and its k\textsubscript{i} rate parameter (32.1 ± 0.2 kJ mol\textsuperscript{-1}). The larger values observed at high temperatures reflect the more prevalent contributions from recombinative desorption routes (reverse of steps 1.1–1.3) and the higher desorption energies as H*/D* coverages decrease with increasing temperature.

These temperature trends and the similar \( \frac{r_{\text{HD},f}(H_2) + (D_2)}{(H_2)(D_2)} \) values below 700 K (Figure 7a) demonstrate that H\textsubscript{2}–D\textsubscript{2} isotopic exchange at relevant dihydrogen pressures (>5 kPa H\textsubscript{2}) occurs almost exclusively via reactions between H\textsubscript{2} and D* (or D\textsubscript{2} and H*) (steps 1.4–1.5, Scheme 1); these routes avoid the need to desorb H* or D* from equilibrated H*/D* adlayers as part of each exchange turnover. Consequently, the reversibility of dissociative dihydrogen adsorption and H*/H\textsuperscript{−} (or H\textsuperscript{−}–D*, D*/D\textsuperscript{−}) recombination (steps 1.1–1.3, Scheme 1) during hydrogenation–dehydrogenation catalysis cannot be determined solely from H\textsubscript{2}–D\textsubscript{2} isotopic exchange rates during catalysis.

### 3.5. Effect of Catalyst Support and Particle Size on Isotopic Exchange Rates

H\textsubscript{2}–D\textsubscript{2} isotopic exchange rates were measured on 0.2% wt. Pt/SiO\textsubscript{2}-A, 0.2% wt. Pt/SiO\textsubscript{2}-B, and 1% wt. Pt/γ-Al\textsubscript{2}O\textsubscript{3}-A at temperatures between 303 and 433 K in order to examine the effects of the support and Pt nanoparticle diameter (1.5–3.2 nm) on exchange rates and activation energies. Rates were also measured on unsupported Pt powders (mean diameter of 374 nm). These latter samples sintered significantly during pretreatments at 873 K (Section 2.3), leading to a reduction in surface area available for catalytic turnovers. The small amount of Pt powders (ca. 0.0005 g) used in kinetic studies and the low surface area following such sintering were not amenable to surface area measurements by N\textsubscript{2} adsorption methods; reported rates and mean particle diameters in Pt powder samples were therefore calculated by assuming that the turnover rates on these catalysts were identical to those on Pt/SiO\textsubscript{2}-A at 383 K (171 ± 2 s\textsuperscript{-1}; 20 kPa H\textsubscript{2}, 20 kPa D\textsubscript{2}). Figure 8 shows \( \frac{r_{\text{HD},f}(H_2) + (D_2)}{(H_2)(D_2)} \) activatio...
Table 2. Dispersion, Mean Nanoparticle Diameter, H2−D2 Exchange Rate, and Activation Energies of Pt/SiO2-A, Pt/Al2O3-A and Pt/γ-Al2O3-A

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Pt dispersion</th>
<th>nanoparticle diameter (nm)</th>
<th>H2−D2 exchange rate (s−1)</th>
<th>H2−D2 exchange activation energy (kJ mol−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SiO2-A</td>
<td>0.38</td>
<td>3.2</td>
<td>171 ± 2</td>
<td>32.1 ± 0.2</td>
</tr>
<tr>
<td>Pt/Al2O3-A</td>
<td>1.0</td>
<td>1.5</td>
<td>183 ± 4</td>
<td>30.1 ± 0.2</td>
</tr>
<tr>
<td>Pt/γ-Al2O3-A</td>
<td>0.72</td>
<td>1.9</td>
<td>205 ± 11</td>
<td>29.3 ± 0.1</td>
</tr>
<tr>
<td>Pt black</td>
<td>~0.003d</td>
<td>374</td>
<td>171d</td>
<td>27.2 ± 0.3</td>
</tr>
</tbody>
</table>

*CALCULATED BY ASSUMING HEMISPHERICAL PARTICLE GEOMETRIES AND USING THE BULK DENSITY OF Pt (21.45 g cm−3).*52 H/pt stoichiometries were estimated using eqs 4 and 5.52 Measured at 383 K, 20 kPa H2, and 20 kPa D2.52 Calculated for temperatures between 303 and 433 K (20 kPa H2 and 20 kPa D2).52 Rates and dispersion of Pt black calculated by assuming negligible particle size effects and equating its exchange activity with that of Pt/SiO2-A at 383 K.

“Calculated by assuming hemispherical particle geometries and using the bulk density of Pt (21.45 g cm−3).”52 H/pt stoichiometries were estimated using eqs 4 and 5.52 Measured at 383 K, 20 kPa H2, and 20 kPa D2.52 Calculated for temperatures between 303 and 433 K (20 kPa H2 and 20 kPa D2).52 Rates and dispersion of Pt black calculated by assuming negligible particle size effects and equating its exchange activity with that of Pt/SiO2-A at 383 K.

The kinetic dependence of H2−D2 isotopic exchange on H2 and D2 pressures (5−40 kPa) was also measured on Pt/γ-Al2O3-A and Pt black at 383 K, as on Pt/SiO2-A (Figure 4). HD formation rates on Pt/γ-Al2O3-A and Pt black increased monotonically with H2 and D2 pressures at all pressures (Figure 9) and, as in the case of Pt/SiO2-A (Figure 4), were essentially the same when H2 and D2 pressures were switched (Figure 9, as indicated by significant overlap between open and closed symbols of the same type). Thus, isotopic exchange rates are well described by eqs 19 and 20 (Figure 10), as in the case of Pt/SiO2-A (Figure 6; Section 3.2).

The values of k−2 and k0 on Pt/SiO2-B and Pt black at 383 K are listed in Table 3. The k−2 values were essentially 0 on Pt/γ-Al2O3-A (−5 ± 40 s−1) and Pt black (−9 ± 49 s−1), as also found on Pt/SiO2 (−2.1 ± 20 s−1), indicative of negligible contributions from recombinative desorption routes (Scheme 1, steps 1.1−1.3). The value of k0 on Pt/γ-Al2O3-A (10.3 ± 0.6 kPa−1 s−1); H or D reactions with D* and H* adatoms; Scheme 1, steps 1.4−1.5) is similar to that measured on Pt/SiO2-A (9.1 ± 0.2 kPa−1 s−1), within experimental uncertainty, consistent with undetectable effects of nanoparticle size (1.9 vs. 3.2 nm for Pt/γ-Al2O3-A and Pt/SiO2-A, respectively; Table 2) on exchange turnover rates.48 The near-identical activation energies (Figure 8) and kinetic trends on Pt black and Pt/SiO2 (Figures 4 and 9) indicate that H2−D* and D2−H* exchange events are not mediated (or affected) by any hydrogen-spillover phenomena that could involve migration of H atoms dissociated on Pt nanoparticles to exchange sites on supports.52 The similar kinetic trends with H2 and D2 pressure on Pt/SiO2-A, Pt/γ-Al2O3-A, and Pt black samples (Figures 4 and 9) are consistent with a similar single-site non-competitive adsorption mechanism, in which H2 adsorbs and reacts with D* (or D2 with H*) via steps that are not significantly affected by changes in surface structure induced by varying nanoparticle size or the nature of the support (Table 3).

3.6. Theoretical Treatments of H2−D2 Exchange Elementary Steps on Pt Surfaces at Near-Saturation Hydrogen Coverages. The kinetic trends described above can identify the involvement of specific routes and the absence of others, but they are not able to discern the precise interactions and geometries involved in the formation of the transition states that mediate H2−D* (and D2−H*) reactions at the prevalent H* (and D*) coverages. More specifically, the “non-competitive” nature of the H2 “binding” at the isotopic exchange transition state for H2 reactions with D* may involve reactions such as (i) a gaseous H2 molecule; (ii) a physisorbed H2 molecule interacting weakly with the D* adlayer; or (iii) a H2 molecule interacting with “spaces” made available within D*(H*) adlayers, but without requiring the prior desorption of a chemisorbed D* atom. The first two routes are those proposed from measured kinetic data in previous studies.25−32 All three routes would lead to rates described by the same rate equation (eq 19, second term) and by the molecularity of the elementary reactions depicted as steps 1.4−1.5 (Scheme 1).

Theoretical methods (DFT) are used to describe the nature of the H* adlayers on Pt surfaces, the interactions among H2-derived species and these adlayers, and the plausible intermediates and transition states that mediate the exchange of H atoms between a H2 molecule and a bound H*. H* atoms formed via H2 dissociation events can bind to atop, bridge, and...
two distinct (fcc and hcp) threefold sites on Pt(111) surfaces. Atp and threefold sites bind H* with similar adsorption enthalpies (−18 and −21 kJ mol−1 at 1 H*/Pt). Their small differences in binding energy lie within the inaccuracies of DFT, and the available infrared and thermal desorption data cannot unequivocally discern a preference for one of these binding modes.59–61 H2−H* exchange reactions are thus examined on surfaces saturated with H* atoms (H*/Pt = 1) present in either atop or fcc binding modes prior to exchange; such exchange reactions can be probed using H2−H* exchange (instead of H2−D*) because theoretical treatments are able to trace individual atoms throughout the reaction coordinate. Calculations of H2−D* and D2−H* reactions on D*-, and H*-covered surfaces, respectively, were also performed to calculate KIE values. H2−H* exchange reactions were also assessed on 201-atoms Pt nanoparticle models (Pt201, 1.8 nm). Such particles exhibit diameters similar to the synthesized samples (Table 1), and the structural model used (flat extended surface vs curved nanoparticle) influences DFT-derived activation barriers for reactions of bound species (e.g., ethane hydrogenolysis on H*-covered metal particles55) and the adsorption enthalpies and saturation coverages for H*, CO54,62–64, NO65,66 on Ru, Rh, Ir, and Pt catalysts. Pt201 nanoparticles bind H* adatoms at atop or fcc sites within their (111) terraces and at a mixture of bridge and atop sites along edges, corners, and (100) terraces; such nanoparticles can achieve H*/Pt ratios larger than unity (SI-7 and previous studies41,67–70). H2−H* exchange reactions were therefore also examined for a range of coverages (1−1.8 H*/Pt) on the Pt(111) terraces of Pt201 particles and compared with the results obtained from Pt(111) surface models.

DFT-derived enthalpy and free-energy barriers for H2−H* exchange are used here to assess the relative contributions of the different mechanisms that can account for observed exchange rates. Measured kinetic effects of H2 and D2 pressures on exchange rates (Section 3.3) below 700 K are consistent with these single-site routes (steps 1.4−1.5, Scheme 1) but not with recombinative desorption events as the prevalent route (steps 1.1−1.3, Scheme 1). These single-site routes (steps 1.4−1.5, Scheme 1) involve measured activation barriers of 29−32 kJ mol−1 (k4; Table 2; range reflects barriers measured on different catalysts) on Pt nanoparticles saturated with H* and D*. The elementary steps in Scheme 1 implicate the involvement of a dihydrogen molecule that does not compete for surface sites (●) with the H* (or D*) species present at near-saturation coverages and with the reaction of such dihydrogen molecules with H* (or D*).

One plausible route for H2−H* reactions involves a metallocycle transition state (TS) (Figure 11a) with a formation enthalpy of 205 kJ mol−1 (from H2(g) and a H* on a H*-covered (atop) Pt(111) surface). This activation barrier is much larger than measured values (29−32 kJ mol−1; Table 2), a consequence of the unstable nature of the H atoms in the metallocycle TS that do not interact with the Pt surface. A dual-site metallocycle-mediated exchange mechanism involving H−H dissociation across a H*−H* pair (Figure 11b) gave a barrier of 147 kJ mol−1. This barrier is smaller than that for single-atom metallocycles (210 kJ mol−1, Figure 11a) but remains about 100 kJ mol−1 larger than measured values (29−32 kJ mol−1, Table 2); this dual-site metallocycle route also predicts kinetic trends (derived in SI-3.2) that contradict the observed effects of H2 and D2 pressures on exchange rates. For H* species bound at fcc sites on Pt(111), no single-site metallocycle transition state could be isolated, and the barrier for the dual-site metallocycle route (140 kJ mol−1) was only slightly smaller than that for H* at atop sites. These high activation barriers for metallocycle-mediated routes indicate that the H2 species must interact with the Pt surface in order to exchange one of its H atoms with H* with barriers resembling those observed experimentally; the measured kinetic trends (described by the second term in eq 19; Section 3.3) dictate that such direct interactions cannot require the intervening desorption of H* (or D*) from saturated surfaces.

Such H2−Pt interactions and the dissociation of H2 molecules may be facilitated by displacing H* adatoms to alternate binding sites (e.g., from atop to fcc) to create “space” for H2−Pt interactions at the TS forms. H2 can thus react in a “sequential” manner, in which H2 dissociates to form a locally
supersaturated H* adlayer, and two nearby H* recombine to form H2 (shown for H2−D2 reactions in Scheme 2). The rate of HD formation from Scheme 2 (derivation in SI-8) is given by

\[ r_{HD} = k'_{-2} \frac{(H_2)(D_2)}{((H_2) + (D_2))^2} + 2k'_{-1} \frac{(H_2)(D_2)}{(H_2) + (D_2)} \]

Equation 22 was derived by assuming the absence of KIEs (consistent with measured KIE values of 1.1 ± 0.3, Section 3.3) and that the atop sites (*) are saturated while the fcc sites (′) are mostly bare. Equation 22 is identical in form to eq 19 and therefore consistent with the exchange rates reported in Section 3.3.

The activation barriers for H2 dissociation and H*−H′ recombination depend on the distance between the displaced H* adatom and the H2 dissociation transition state. The enthalpy barriers for H2 dissociation (referenced to a H* (atop)-covered Pt surface; 1 H*/Pt) are 79 kJ mol\(^{-1}\) when the H* atom moves from an atop site to a vicinal bridge site (Figure 11c), 65 kJ mol\(^{-1}\) when H* moves to an adjacent fcc site (Figure 11d), and 55 kJ mol\(^{-1}\) when it moves to an fcc site that is not neighboring the metal site involved in H2 dissociation (Figure 11e). The enthalpy barriers for H2−H* exchange on H* adlayers in the fcc binding mode vary from 101 to 116 kJ mol\(^{-1}\) via reactions in which H* atoms shift from fcc to atop sites in order to accommodate the H2 dissociation transition state (Figure S10 in SI-9). These barriers on fcc-dominated H* adlayers are much larger than those on atop-dominated adlayers. The lowest-enthalpy path involves displacement of H* from atop sites to fcc sites to facilitate H2 dissociation; however, the activation enthalpies (54–79 kJ mol\(^{-1}\)) of this path remain 25–50 kJ mol\(^{-1}\) larger than measured values at low temperatures (<700 K) for Pt/SiO2-A, Pt/SiO2-B, and Pt/γ-Al2O3-A (29–32 kJ mol\(^{-1}\), Table 2).

Previous DFT studies of other reactions (e.g., ethane hydrogenolysis on Ir(111) surfaces) at high H* coverages showed that larger-sized surface models (e.g., 6 × 6 instead of...
on Pt Surfaces

$\text{H}_2 + 2^* \rightleftharpoons 2\text{H}^*$  \hspace{1cm} [2.1]

$\text{HD} + 2^* \rightleftharpoons \text{H}^* + \text{D}^*$ \hspace{1cm} [2.2]

$\text{D}_2 + 2^* \rightleftharpoons 2\text{D}^*$ \hspace{1cm} [2.3]

$\text{H}_2 + \text{H}^* + \cdot \rightleftharpoons \text{H}^* + \text{H}^* + \text{H}^*$ \hspace{1cm} [2.4]

$\text{H}_2 + \text{D}^* + \cdot \rightleftharpoons \text{D}^* + \text{H}^* + \text{H}^*$ \hspace{1cm} [2.5]

$\text{HD} + \text{H}^* + \cdot \rightleftharpoons \text{H}^* + \text{H}^* + \text{D}^*$ \hspace{1cm} [2.6]

$\text{HD} + \text{D}^* + \cdot \rightleftharpoons \text{D}^* + \text{H}^* + \text{H}^*$ \hspace{1cm} [2.7]

$\text{HD} + \text{D}^* + \cdot \rightleftharpoons \text{D}^* + \text{D}^* + \text{H}^*$ \hspace{1cm} [2.8]

$\text{D}_2 + \text{H}^* + \cdot \rightleftharpoons \text{H}^* + \text{D}^* + \text{D}^*$ \hspace{1cm} [2.9]

$\text{D}_2 + \text{D}^* + \cdot \rightleftharpoons \text{D}^* + \text{D}^* + \text{D}^*$ \hspace{1cm} [2.10]

$\text{D}_2 + \text{D}^* + \cdot \rightleftharpoons \text{D}^* + \text{D}^* + \text{D}^*$ \hspace{1cm} [2.11]

These trends in DFT-derived barriers with cell size (Table 4) reflect the inability of flat periodic surfaces to accommodate disruptions within their adlayer as previously described for other reactions and adsorbates; this suggests that $\text{H}_2$ exchange reactions on non-periodic Pt particle models may represent a more faithful description of experimental systems at near-saturation coverages. $\text{H}^*$ adatoms bind to atop or fcc sites (Figures S7–S9 in SI-7) on low-index (111) facets of Pt$_{201}$ nanoparticles with similar adsorption energies for the two adlayers over a range of coverages (1.4–1.7 $\text{H}^*/\text{Pt}_6$), as in the case of Pt(111) surfaces (at 1 $\text{H}^*/\text{Pt}_6$). On corners, edges, and (100) facets, $\text{H}^*$ binds in a mixture of bridge and atop modes that depends on $\text{H}^*$ coverage. Measured $\text{H}_2$-$\text{D}_2$ exchange rates were insensitive to the size of Pt nanoparticles (Table 2), which changes the mean coordination of exposed Pt atoms; these observations indicate that exchange reactions do not occur preferentially at the corner and edge Pt atoms that become more prevalent on smaller nanoparticles. $\text{H}_2$-$\text{H}^*$ exchange steps were examined $\text{H}^*$-covered (111) terraces on Pt$_{201}$ which provides a direct comparison to Pt(111) surface models, with $\text{H}^*$ atoms located in atop or fcc binding modes and at different total $\text{H}^*$ coverages (1.15–1.93 $\text{H}^*/\text{Pt}_6$); supratwo-dimensional coverages (1.0 $\text{H}^*/\text{Pt}_6$) were achieved by varying the number of $\text{H}^*$ bound to the corner and edge Pt atoms at the boundaries of the (111) terraces. The enthalpy barrier for $\text{H}_2$ dissociation is 35 kJ mol$^{-1}$ at 1.15 $\text{H}^*/\text{Pt}_6$ when displacing $\text{H}^*$ to a nearby (but not adjacent) fcc site (Figure 12b), a value that is similar to that obtained for 6 $\times$ 6 cells on Pt(111) surfaces (39 kJ mol$^{-1}$). Differential adsorption energies of $\text{H}^*$ increase with increasing $\text{H}^*$ coverage but remain negative at coverages as high as 1.44 $\text{H}^*/\text{Pt}_6$ and become positive at 1.7 $\text{H}^*/\text{Pt}_6$. This suggests that small Pt particles saturate at coverages above 1.0 $\text{H}^*/\text{Pt}_6$ (SI-7), as shown previously. At the expected coverage of 1.44 $\text{H}^*/\text{Pt}_6$ based on differential adsorption enthalpies (SI-7), the barriers are 27 kJ mol$^{-1}$, very close to the measured values (29–32 kJ mol$^{-1}$, Table 2). The $\text{H}_2$-$\text{H}^*$ exchange activation barriers range from 27 to 58 kJ mol$^{-1}$ for different coverages within $\text{H}^*$ adlayers (at 1.15–1.93 $\text{H}^*/\text{Pt}_6$) that have $\text{H}^*$ bound at atop sites within their (111) terraces (Figure 12a). Higher barriers (57 and 50 kJ mol$^{-1}$) at coverages of 1.74 and 1.93 $\text{H}^*/\text{Pt}_6$ are likely irrelevant to experimental conditions because such coverages are unlikely to be present based on the differential adsorption energies (SI-7).

Larger barriers were measured at temperatures greater than 700 K; these barriers may reflect the recombative pathway (steps 1.1–1.3, Scheme 1) and the increase in the enthalpy of desorption with decreasing $\text{H}^*$ (or $\text{D}^*$) coverage as the temperature increases. DFT-based comparisons of the $\text{H}^*$-displacement (Scheme 2) and recombative pathways, however, give inaccurate results because of the large errors in DFT-derived entropies for $\text{H}^*$, as shown in earlier studies.

The barriers for $\text{H}^*$-displacement mechanisms on (111) terraces of Pt$_{201}$ particles that have fcc-bound $\text{H}^*$ are larger than those with atop-bound $\text{H}^*$, with barriers of 74–87 kJ mol$^{-1}$ for $\text{H}_2$-$\text{H}^*$ exchange at 1.38–1.67 $\text{H}^*/\text{Pt}_6$ by displacing $\text{H}^*$.

Table 4. $\text{H}_2$-$\text{H}^*$ Reaction Enthalpy Barriers, Free-Energy Barriers, and KIE Values on Pt(111) Surfaces of Varying Supercell Sizes (3 $\times$ 3, 4 $\times$ 4, and 6 $\times$ 6) and $\text{H}^*$ Displacement Locations

<table>
<thead>
<tr>
<th>supercell size</th>
<th>displaced $\text{H}^*$ location</th>
<th>enthalpy barrier (kJ mol$^{-1}$)</th>
<th>free-energy barrier (kJ mol$^{-1}$)</th>
<th>KIE$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 $\times$ 3</td>
<td>adjacent fcc</td>
<td>67</td>
<td>114</td>
<td>1.60–1.37</td>
</tr>
<tr>
<td></td>
<td>farther fcc</td>
<td>57</td>
<td>104</td>
<td>1.50–1.25</td>
</tr>
<tr>
<td>4 $\times$ 4</td>
<td>adjacent bridge</td>
<td>79</td>
<td>132</td>
<td>1.38–1.28</td>
</tr>
<tr>
<td></td>
<td>adjacent fcc</td>
<td>65</td>
<td>113</td>
<td>1.59–1.31</td>
</tr>
<tr>
<td></td>
<td>farther fcc</td>
<td>55</td>
<td>104</td>
<td>1.46–1.18</td>
</tr>
<tr>
<td>6 $\times$ 6</td>
<td>adjacent fcc</td>
<td>48</td>
<td>90</td>
<td>1.40–1.49</td>
</tr>
<tr>
<td></td>
<td>farther fcc</td>
<td>39</td>
<td>82</td>
<td>1.30–1.35</td>
</tr>
</tbody>
</table>

$^a$KIE ratios depend on the isotopic identity of spectating $\text{H}^*$ (or $\text{D}^*$) in the adlayer; thus, a range is provided which describes KIE of rate constants for $\text{H}_2$-$\text{D}^*$ (single $\text{D}^*$ on $\text{H}^*$ adlayer) to $\text{D}_2$-$\text{H}^*$ (single $\text{H}^*$ on $\text{D}^*$ adlayer) and for $\text{H}_2$-$\text{D}^*$ (all $\text{D}^*$ adlayer) to $\text{D}_2$-$\text{H}^*$ (all $\text{H}^*$ adlayer).
an fcc H* to an atop H* site to make room on the catalyst surface for H2 dissociation (Figure S11 in SI-9). These trends demonstrate that fcc-dominant H* adlayers are less reactive than atop-based H* adlayers for H2–H* exchange and that both atop and fcc adlayers on Pt201 nanoparticle models avoid the steric hindrance to lateral relaxation imposed by small (3 × 3, 4 × 4) periodic Pt(111) models as H* is displaced to an alternate binding site in order to accommodate the H2 dissociation TS.

Experimental KIE values (k/d/ki; Scheme 1) were calculated from kinetic data by comparing rate ratios (k/d; eq 16; Figure S, Section 3.3). For instance, the HD formation rates at 40 kPa H2 and 5 kPa D2 and at 5 kPa D2 and 40 kPa H2 led to a rate ratio of 1.01 ± 0.11 (Figure S). Such ratios near unity when H2/D2 molar ratios were inverted were used to infer that HD formation pathways have KIE values near unity (Section 3.3). Scheme 2, however, shows that HD can form via several pathways (steps 2.6–2.9), each plausibly exhibiting different rate constants. Measurements reflect the appropriate ensemble average over all possible routes forming HD (steps 2.6–2.9; Scheme 2) and all steps that determine the coverages of H*, D*, H’, and D’ (steps 2.4–2.11; Scheme 2). DFT methods are able to assess KIEs for each step; these require, however, a large number of calculations for all binding locations and combinations of isotopes. As a result, KIE values are estimated for only two representative exchange reactions (H2–D* and D2–H*; steps 2.5 and 2.10), which are also included in Scheme 1 (steps 1.4–1.5); these KIE values (k/d/kf, Scheme 2; k/d/kf, Scheme 1) were obtained by calculating the free-energy barriers for H2–D* and D2–H* reactions on Pt(111) surfaces and Pt201 catalyst models while varying H*/D* ratios in the rest of the adlayer (consisting of spectating H* or D* atoms).

The free-energy barriers for H2–D* reactions where D* is displaced to a “farther” fcc site (Figure 11e) vary from 104.8 kJ mol⁻¹ to 105.1 kJ mol⁻¹ on a 3 × 3 Pt(111) surface as the isotopic contents of the spectating adlayer vary from only H* to only D*. The barriers for D2–H* reactions vary from 105.8 to 106.1 kJ mol⁻¹ for the same isotopic content range in the spectating adlayer. These data lead to differences in free-energy barrier (∆ΔG) values between these two exchange reactions of ~1 kJ mol⁻¹, favoring H2–D* exchange; they lead to KIE values (k/d/kf, Scheme 2; k/d/kf, Scheme 1) of 1.4 for all adlayer isotopic contents. Experimental KIE values, however, were estimated by measuring rates under inverse pressure conditions (Figure 5); thus, k/d/kf (Scheme 2) and k/d/kf (Scheme 1) were also calculated by comparing free energies for H2–D* and D2–H* reactions while also swapping the isotopic content of the spectating adlayer. Using this approach, the k/d/kf (Scheme 2) and k/d/kf (Scheme 1) values range from 1.50 when comparing H2–D* (with D* in all spectating positions) and D2–H* (with H* in all spectating positions) to 1.25 when comparing H2–D* (with H* in all spectating positions) and D2–H* (with D* in all spectating positions). These KIE values from 1.25 to 1.50 lie within the experimental uncertainty (1.1 ± 0.3; Section 3.3). This same exchange mechanism (Figure 11e) was examined on larger 4 × 4 and 6 × 6 cells on Pt(111) surfaces. The KIE values on these larger periodic cells are typically closer to unity than for 3 × 3 cells; they give KIE ranges of 1.18–1.46 for 4 × 4 and 1.30–1.35 for 6 × 6 surfaces, where the ranges reflect different isotopic compositions within the spectating adlayer. DFT-derived KIE values for H2–D* and D2–H* steps on Pt201 nanoparticle surfaces were essentially independent of H* and D* combined coverages (1.15–1.93 H*/Pt2; 1.25–1.43 KIE values). These KIE ranges are consistent with measured values (1.1 ± 0.3, Section 3.3).

DFT methods indicate that H2–D2 exchange occurs predominantly via non-competitive adsorption routes at the temperatures of the kinetic measurements (300–700 K; Section 3.3) in which H2 (or D2) displaces D* (or H*) atoms to create spatial access to the Pt surface atoms for dissociation events. Such pathways do not require the intervening removal of D* (or H*) from equilibrated adlayers via recombinative desorption but lead instead to the temporary

Figure 12. (a) DFT-calculated reaction enthalpy barriers (relative to H2 in the gas phase and a H*-covered surface) for H2–H* reactions on Pt201 particles (at varying H* coverages) (●) when displacing H* from a top site to a farther fcc site [fcc-dominant surfaces, (b–c)] and on Pt201 particles (■) when displacing H* from an fcc site to a top site (fcc-dominant surfaces, SI-7). Atoms highlighted in orange reflect those from gas-phase H2 and those highlighted in green reflect H* atoms displaced to adjacent binding modes to accommodate the H2 dissociation transition states. KIE values reflect the differences in rate constants for H2–D* and D2–H* reactions; ranges reflect changing the isotopic composition of the spectating adlayer.

https://doi.org/10.1021/acs.jpcc.1c09131
J. Phys. Chem. C 2022, 126, 3923–3938
local supersaturation of the Pt surface and to a decrease in the H*/D* binding energy at such locations; H*−D* (or D*−H*) recombine to form HD(g), thus completing an exchange turnover. The non-competitive adsorption of H2 (and D2) through adatom displacements disrupts the H*/D* adlayer in a manner that allows H2−D2 exchange to occur at much faster rates than expected from recombinative desorption from equilibrated adlayers, from which recombinative desorption occurs with higher barriers (78 ± 11 kJ mol−1; Section 3.4) than from locally supersaturated surfaces (39−57 kJ mol−1; Table 4). Activation enthalpies decrease as the surface model includes a larger number of Pt atoms for periodic Pt(111) surfaces. Such trends indicate that the exchange TS creates adlayer strain through interactions among TS structures in adjacent cells. Nanoparticle models lack such artifacts of adlayer strain through interactions among TS structures in (111) terraces. Periodic and nanoparticle surface models show that H* adlayers with H* in atop binding modes on (111) surfaces (or terraces) give smaller exchange barriers than adlayers in which H* binds at fcc sites, giving better agreement between the former atop-dominated adlayers and the measured kinetic behavior. Activation free energies that determine KIE are essentially independent of the spectating adlayer isotopic content and are also nearly the same for H2−D* or D2−H* exchange events, leading to DFT-derived KIE values near unity (near 1.3), consistent with experimental results.

4. CONCLUSIONS

H2−D2 exchange reactions are frequently employed in mechanistic studies to probe the reversibility of H2 dissociative adsorption reactions without proper considerations for the thermodynamics of H2 versus D2 adsorption or the mechanism by which isotopic exchange events occur. In this study, uptakes of H2 and D2 were measured on several Pt-based catalysts to determine TIE values at temperatures (523−673 K) relevant for catalytic hydrogenation/dehydrogenation reactions. These TIE values were near unity and depended only weakly on the temperature of adsorption, corresponding with a 4 kJ mol−1 difference in the dissociative adsorption enthalpy for H2 and D2. Such temperature dependences were used to calculate H* and D* equilibrium coverages at the temperatures of H2−D2 exchange kinetic studies. These coverages and the kinetic dependences of exchange on H2 and D2 pressures at 373 K were shown to be inconsistent with the commonly proposed recombinative desorption pathway. H2−D2 exchange reactions instead occur predominantly via single-site reactions between H2 and D* (or D2 and H*) for temperatures below 700 K. Isotopic exchange rates were also nearly identical when H2 and D2 pressures were swapped, reflecting the absence of a KIE and an adlayer whose composition is determined by H2−D* or D2−H* exchange reactions rather than the thermodynamics (and TIE) of H2 and D2 dissociative adsorption. Theoretical calculations showed that these exchange reactions are mediated instead by the non-competitive adsorption and dissociation of H2 or D2 onto Pt surfaces at spaces created from the displacement (but not desorption) of H* and D* adatoms to alternate binding modes. Activation enthalpies decreased in these calculations as the catalyst model became larger for Pt(111) surfaces and were lower on Pt nanoparticle models than on periodic surface models, indicating that these exchange transition states cause adlayer strain via through-adlayer interactions in neighboring unit cells within the periodic models. Calculated activation enthalpy barriers and KIE values on the largest surface (6 × 6 Pt(111)) models and on nanoparticle models were in close agreement with experimental values. The results from this study thus demonstrate that H2−D2 isotopic exchange are mediated by reaction pathways that bypass dissociation–recombination reactions at low temperature and therefore cannot be used to conclusively demonstrate the reversibility of H2 dissociative adsorption reactions on catalytic surfaces.

■ ASSOCIATED CONTENT

+ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c09131.

Effect of catalyst pellet size on reaction rates; H2 and D2 chemisorption isotherms on Pt/γ-Al2O3-B at 523−673 K; derivation of rate equations for H2−D2 exchange mechanisms; parity plots of H2−D2 exchange models; calculation of exchange rates simulating various magnitudes of KIEs for H2−D2 exchange; sensitivity analysis of rate parameters k−1 and k4; DFT-derived hydrogen adsorption enthalpies as a function of coverage on Pt(111) surfaces and Pt201 particles; derivation of rate equations for DFT-derived H2−D2 exchange mechanism; and DFT-derived transition states and enthalpy barriers for H*−H* reactions in H*(fcc)-dominated adlayers on Pt(111) surfaces and Pt201 particles (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Enrique Iglesia — Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720, United States; orcid.org/0000-0003-4109-1001; Phone: (510) 642-9673; Email: iglesia@chem.berkeley.edu; Fax: (510) 642-4778

Authors

Samuel L. Leung — Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720, United States; orcid.org/0000-0002-0915-1361

David Hibbitts — Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, United States; orcid.org/0000-0001-8606-7000

Monica García-Díezuez — Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720, United States; Present Address: Johnson Matthey, Billingham, TS23 1LB, United Kingdom

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.1c09131

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was funded by Chevron Corporation. S.L.L. acknowledges funding from a Chevron Graduate Student Research Fellowship. We also thank Dr. Aaron Sattler for helpful technical discussions.
Additional Notes

$^\text{1}$N$_2$ is used as the inert carrier and internal standard in place of He to avoid overlap with the D$_2$ 4 amu signal in the mass spectra.

$^\text{2}$Absolute exchange rates and the value of $k_4$ on Pt black cannot be compared directly because the rates on Pt black were normalized by the rates on Pt/SiO$_2$-A at 383 K.

$^\text{3}$The same functional form arises if the choices of the binding modes are switched.

References


(3) Bugeleisen, J.; Wölfersberg, M. Theoretical and Experimental Aspects of Isotope Effects in Chemical Kinetics; Advances in Chemical Physics; Wiley Online Library, 1958;Vol. 1, pp 15–76. DOI: 10.1002/9780470143476.ch2


(18) Ozaki, A. Isotopic Studies of Heterogeneous Catalysis; Kodansha, 1977.


(43) Hanson, R. M.; Green, S. M. E. Introduction to Molecular Thermodynamics; University Science Books: Sausalito, Calif., 2008.


