Elementary Steps in D₂–H₂O and H₂–D₂–H₂O Exchange Reactions on Pt Nanoparticles and Consequences of Liquid Water for the Binding and Reactivity of Chemisorbed Hydrogen

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1. INTRODUCTION

Surface catalysis involves the binding of reactants, their chemical transformations, and the ultimate desorption of the products formed.1 Understanding the nature of bound species and binding sites and the consequences of outer-sphere environments, such as a contacting liquid phase, is essential to interpret and design specific reaction channels for bound molecules. Dihydrogen dissociation and the reactions of bound H atoms (H*) mediate many useful reactions,2−4 such as hydrogcnolysis of alkanes5−7 and hydrogenation of alkenes,8−10 amines,11−13 and CO.14−17 These processes have been probed using chemisorption,18,19 calorimetry,20−22 spectroscopy,14,23,24 electrochemistry,25−28 low-energy electron diffraction,29,30 density functional theory (DFT),31−53 and isotopic exchange methods.34−37 These inquiries have addressed H-binding thermodynamics and H₂ dissociation dynamics in the absence of adsorbed species and also in the presence of alkanes,5,41 CO,42,43 and water.14,27,34

Isotopic exchange, as a method of inquiry, is useful to identify and probe the reversibility and kinetic relevance of elementary steps and to do so without disrupting the chemical steady state, thus providing uncorrupted, albeit indirect, details about the nature and prevalence of bound species and binding sites. The accurate interpretation of these data requires mechanistic insights into the elementary steps and their thermodynamics. The mechanism of H₂O−D₂ (or D₂O−H₂) isotopic exchange on Pt surfaces has been addressed in previous studies14,27,34,44,45 but without rigorous mechanistic interpretations of exchange rates or any simultaneous assessments of the binding thermodynamics of bound species derived from H₂, D₂, and H₂O. In addition, the presence of trace contaminants in H₂O (as chemical impurities or dissolved gases) emerged in the present study as a potential ubiquitous corruption of previously reported exchange rates.

Received: July 11, 2023
Revised: September 29, 2023
Accepted: October 3, 2023
Published: November 1, 2023
The present study addresses these mechanistic and experimental matters. It presents a unifying set of elementary steps that is consistent with all available kinetic and thermodynamic data, including insights and data from a previous study of H$_2$–D$_2$ exchange under anhydrous conditions. The kinetic descriptions derived from these anhydrous data also accurately describe exchange rates in the presence of liquid H$_2$O, without requiring any modifications of the form of the expression or any evidence for effects of water, whether in gaseous, adsorbed, or liquid forms, on the kinetic or thermodynamic parameters involved in the reactions of chemisorbed H atoms (H* and D*). Such results reflect the minor consequences of liquid water as a solvent for the binding of H*/D* species and the transition states (TS) that mediate H$_2$–D$_2$ exchange.

Dissolved gases in liquid water can lead to unintended titration of metal surfaces. Their incomplete removal from reagents irreversibly affects exchange rates; these effects persist even after removing H$_2$O from the reactant stream. CO$_2$ is particularly challenging to remove through routine degassing protocols involving evaporation or extended flow of inert gases because it is present as solvated carbonate and bicarbonate ions. When released into an inlet stream during the vaporization of liquid H$_2$O, gaseous CO$_2$ dissociates on metal surfaces at near ambient temperatures to form strongly bound CO (CO*) and O*; the latter can be removed during contact with H$_2$ at near ambient temperature, but CO* (and its C* and O* dissociation products) requires significantly higher temperatures, thus leading to the irreversible titration of Pt surfaces during H$_2$–D$_2$ exchange on samples in contact with (or previously exposed to) contaminated H$_2$O. The H$_2$O–D$_2$ and H$_2$O–H$_2$–D$_2$ kinetic studies presented here resort to atypically stringent precautions and procedures to remove dissolved CO$_2$.

The kinetics of H$_2$O–D$_2$ isotopic exchange are examined here on dispersed Pt nanoparticles in the presence of water but under conditions that either preclude or cause the formation of an intrapore liquid H$_2$O phase. The observed kinetic trends cannot be described using pathways proposed in earlier studies, in the context of the surfaces saturated with H* and D* that prevail during exchange. These trends indicate instead that HDO/D$_2$O and HD/H$_2$ form via reactions of D$_2$ with H$_2$O*, in steps that displace mobile D* (or H*) adsorbates to alternate binding locations (from atop to fcc), thus allowing D$_2$ to dissociate on “spaces” made accessible by such local displacements and then to exchange with H$_2$O*. These steps and the requisite competitive binding of D* and H$_2$O* are consistent with thermodynamic considerations from previous H$_2$ chemisorption studies, as well as with theoretical and experimental evidence for the elementary steps that mediate H$_2$–D$_2$ exchange. The proposed exchange pathways accurately describe exchange rates for D$_2$–H$_2$O and H$_2$–D$_2$–H$_2$O mixtures throughout a broad range of pressures (5–20 kPa of H$_2$, 10–40 kPa of D$_2$, and 0–20 kPa of H$_2$O); these pathways provide a framework to study the nature of hydrogen binding and reactions in the presence of water, whether in gaseous, physisorbed, or liquid forms.

Liquids impose an outer-sphere environment that can influence the binding of molecules as well as their reactivity, the latter through the preferential solvation of TSs and their relevant precursors. These outer-sphere effects have been implicated in modifications of the electronic properties of surfaces and the binding of molecules involved in surface catalysis. H$_2$O–H$_2$–D$_2$ reactions are used here to assess these effects through the formation of an intrapore liquid H$_2$O phase within γ-Al$_2$O$_3$ voids that contain Pt nanoparticles. These capillary condensation strategies allow a continuous transition from gas-filled to liquid-filled pore environments; they have been previously developed to examine the effects of nonpolar liquids on the reactions of hydrocarbons and oxygenates. The measured H$_2$–D$_2$ exchange rates decreased monotonically as H$_2$O pressures increased, but these kinetic trends were not detectably distorted by the gradual formation of an intrapore liquid phase.

The observed effects of H$_2$O on H$_2$–D$_2$ exchange rates merely reflect the competitive adsorption of H$_2$O* and D* on Pt surfaces without any detectable consequences of a liquid phase for the stability of the bound exchange TSs or any perceptible electronic modification of Pt surfaces upon contact with liquid water. Pt surfaces mediate H$_2$–D$_2$ and H$_2$O–D$_2$ exchange by catalytic D$_2$ dissociation at surfaces made available by local disruptions of dense mobile adlayers; exchange rates depend solely on H$_2$O pressure, irrespective of the physical state of water in the outer-sphere environment that contacts Pt nanoparticles. In all cases, competitive binding is driven by the contacting pressure of H$_2$O, irrespective of the presence or absence of H$_2$O in the liquid state.

2. METHODS

2.1. Catalyst Synthesis Methods. The γ-Al$_2$O$_3$ support (Sasol, CATALOX SBA 200) used to disperse Pt nanoparticles was treated in flowing dry air (0.83 cm$^3$ g$^{-1}$ s$^{-1}$; zero-grade; Praxair) by heating from ambient temperature to 1073 K at 0.083 K s$^{-1}$ and holding for 5 h and then cooling to ambient temperature. Pt/γ-Al$_2$O$_3$ (1% wt. Pt) was prepared by incipient wetness impregnation of this γ-Al$_2$O$_3$ with a H$_2$PtCl$_6$ solution (8% wt. in H$_2$O, 0.26 cm$^3$ g$^{-1}$ γ-Al$_2$O$_3$) and treated overnight in ambient air at 368 K. The sample was then exposed to flowing dry air (1.67 cm$^3$ g$^{-1}$ s$^{-1}$; zero-grade; Praxair), heated from ambient temperature to 873 K (0.083 K s$^{-1}$), and then held for 3 h. After cooling to ambient temperature, the sample was exposed to flowing H$_2$ (1.67 cm$^3$ g$^{-1}$ s$^{-1}$; 99.9999% UHP; Praxair), heated to 1073 K (0.083 K s$^{-1}$), held for 2 h, and treated at ambient temperature in flowing 2% v/v O$_2$ (0.83 cm$^3$ g$^{-1}$ s$^{-1}$; balance H$_2$; certified grade, Praxair) for 0.5 h to passivate Pt nanoparticles before exposure to ambient air. Catalysts were heated in flowing H$_2$ (Praxair, UHP, 99.9999% purity; 100 cm$^3$ g$^{-1}$ s$^{-1}$) to 873 K at 0.083 K s$^{-1}$, held for 2 h, and cooled to the target temperature before exchange experiments. Unsupported Pt powders (nominally 22.7 m$^2$ g$^{-1}$ as provided, Strem Chemicals) were treated in flowing H$_2$ (400 cm$^3$ g$^{-1}$ s$^{-1}$; 99.9999% UHP; Praxair) at 1073 K (0.083 K s$^{-1}$) for 2 h immediately before exchange rate measurements.

2.2. Pt Dispersion Measurements from H$_2$ Chemisorption Uptake. Pt dispersion (defined as the fraction of the total number of Pt atoms residing at nanoparticle surfaces) in Pt/γ-Al$_2$O$_3$ was measured from the H$_2$ uptake after heating the sample (~1 g) to 673 K (0.083 K s$^{-1}$) and holding for 1 h in flowing H$_2$ (0.33 cm$^3$ g$^{-1}$ s$^{-1}$; Praxair, UHP, 99.9999% purity) and then exposing it to dynamic vacuum (to <10$^{-5}$ Pa) at 673 K for 1 h before cooling to 373 K. Uptake values were measured by the sequential dosing of known amounts of H$_2$ into a known sample volume containing the sample at different H$_2$ pressures (1–40 kPa H$_2$). Saturation uptake values were obtained from the uptake values extrapolated to zero pressure.
Figure 1. HD formation rates (20 kPa H\textsubscript{2} and 20 kPa D\textsubscript{2}) normalized by initial rates (\(\gamma_{\text{HD},0}\)) on (●) Pt powders and (□) Pt/γ-Al\textsubscript{2}O\textsubscript{3} at 473 K before, during (shaded region), and after exposure to 20 kPa (a) H\textsubscript{2}O-A and (b) H\textsubscript{2}O-B, treated as described in Section 2.3.

The dispersion of Pt in the Pt/γ-Al\textsubscript{2}O\textsubscript{3} samples measured by these methods was 0.72. This dispersion corresponds with an average crystallite diameter of 1.9 nm, calculated using established methods that account for the suprastoichiometric H/ Pt ratios at edge and corner sites (details in Section SI-1.1).

2.3. H\textsubscript{2}–D\textsubscript{2}, H\textsubscript{2}O–D\textsubscript{2}, and H\textsubscript{2}O–H\textsubscript{2}–D\textsubscript{2} Isotopic Exchange Rates. Isotopic exchange turnover rates (units: s\textsuperscript{-1}; normalized by the number of Pt surface sites) were measured on aggregates (<100 μm) of unsupported Pt powders (0.1–0.5 mg) and Pt/γ-Al\textsubscript{2}O\textsubscript{3} (0.5–5 mg) held on a quartz frit within a U-shaped quartz tube (6.35 mm O.D. and 4 mm I.D.). H\textsubscript{2} (99.999% UHP; Praxair), D\textsubscript{2} (99.8% isotopic enrichment, research-grade; Praxair), and N\textsubscript{2} (99.998%, Praxair) were purified using O\textsubscript{2} and H\textsubscript{2}O traps (VICI Metronics). Inlet molar rates were metered with electronic mass flow controllers (Parker-Porter 200 series).

Deionized H\textsubscript{2}O (>18.0 MΩ cm) was further treated by bubbling inert N\textsubscript{2} at ambient temperature for more than 24 h. This water (denoted as H\textsubscript{2}O-A) contains trace dissolved gases and was therefore treated further by exposing to dynamic vacuum at 363 K for 6 h, until about 80% of the starting liquid volume had evaporated (denoted as H\textsubscript{2}O-B). Such extreme degassing procedures were essential to fully remove dissolved gases, specifically CO\textsubscript{y}, which dissociates to form strongly bound CO at the conditions of the exchange experiments (such strong effects of traces of CO\textsubscript{2} are shown in Sections 3.1 and SI-3). H\textsubscript{2}O (H\textsubscript{2}O-A or H\textsubscript{2}O-B) was injected into the flowing gases at 423 K by using a syringe pump (KD Scientific Legato 200).

The concentrations of all reactants and deuterated species (H\textsubscript{2}, HD, D\textsubscript{2}, H\textsubscript{2}O, D\textsubscript{2}O, H\textsubscript{2}O-D\textsubscript{2}, and N\textsubscript{2}) in the effluent were determined using mass spectrometry (Leybold Inficon Transpector, TSP TH200). H\textsubscript{2}–D\textsubscript{2} exchange rates were calculated from these data and corrected for their approach to the binomial distribution expected at equilibrium\textsuperscript{55} at these reaction temperatures (>473 K) to determine the forward rates without contributions from reverse reactions, thus simplifying the mechanism-based equations derived for exchange rates (details in Section SI-1.2).

Reaction rates on Pt powders were normalized using H\textsubscript{2}–D\textsubscript{2} exchange to measure the number of active sites at 373 K (20 kPa H\textsubscript{2} and 20 kPa D\textsubscript{2}). Turnover rates were assumed to be similar to those on Pt/γ-Al\textsubscript{2}O\textsubscript{3}, based on H\textsubscript{2}–D\textsubscript{2} exchange rates shown to be insensitive to nanoparticle diameters (1.5–3.2 nm) in previous studies.\textsuperscript{37} This approach is necessary because Pt powders sinter significantly\textsuperscript{8}–\textsuperscript{60} during H\textsubscript{2} treatment at 1073 K (Section 2.1); such high-temperature treatments were necessary to ensure that additional structural changes did not occur during the reaction, thus corrupting kinetic studies. The small amount of Pt powders (ca. 0.5 mg) used in these experiments and the low surface area following sintering, required to be able to achieve differential conversions, were not amenable to surface area measurements or to particle size estimates from chemisorption uptake. Larger quantities of Pt powders may sinter to different extents and are therefore not reflective of the effective Pt dispersion detected by H\textsubscript{2}–D\textsubscript{2} exchange. Assuming that H\textsubscript{2}–D\textsubscript{2} isotopic exchange rates can be used as an accurate measure of the active surface area, these Pt powders exhibited a particle diameter of approximately 400 nm (calculated using the methods described in SI-1.1). The absence of transport effects were ruled out by nearly identical activation energies for H\textsubscript{2}–D\textsubscript{2} isotopic exchange on Pt powders and Pt/γ-Al\textsubscript{2}O\textsubscript{3} (27.2 ± 0.3 vs 30.1 ± 0.2 kJ mol\textsuperscript{-1}, respectively) that did not curve in an Arrhenius plot with changes in temperature when varying the catalyst aggregate size, as in our prior study.\textsuperscript{37}

2.4. Textural Properties of γ-Al\textsubscript{2}O\textsubscript{3} and Calculation of H\textsubscript{2}O Adsorption Isotherms. N\textsubscript{2} uptakes on γ-Al\textsubscript{2}O\textsubscript{3} were measured at the normal boiling point of N\textsubscript{2} (77 K; Micromeritics 3Flex Adsorption Analyzer) (Section SI-2). The γ-Al\textsubscript{2}O\textsubscript{3} sample (ca. 100 mg) was treated by heating from ambient temperature to 673 at 0.17 K s\textsuperscript{-1} and holding for 3 h under vacuum before these measurements. The pore size distribution was obtained from these uptake data using the Barret–Joyner–Halenda (BJH) equation,\textsuperscript{61} which considers vapor pressure, molar volume, and surface tension of a liquid for any given molecule. The pore size distribution was obtained from the N\textsubscript{2} uptake at the normal boiling point and then used to estimate the H\textsubscript{2}O uptake (and the extent of intrapore capillary condensation) at 323 K using the BJH equation and the molar properties of H\textsubscript{2}O at 323 K, as reported previously for nonpolar liquids in mesoporous silica\textsuperscript{55} and TiO\textsubscript{2}\textsuperscript{36}. This method provides an estimate of the fraction of the γ-Al\textsubscript{2}O\textsubscript{3} void volume that is filled with liquid H\textsubscript{2}O at
3. RESULTS AND DISCUSSION

3.1. Effects of Dissolved CO$_2$ in H$_2$O on H$_2$–D$_2$ Isotopic Exchange Rates. Ultrapure water, free of any traces of CO$_2$, is essential to obtain uncorrupted isotopic exchange rate data and to prevent inaccurate mechanistic assignments because CO$_2$ acts as a precursor to stoichiometric titrants (CO and its dissociation products) of nanoparticle surfaces at low temperatures. These artifacts are demonstrated here by comparing the results with H$_2$O treated using customary degassing protocols (Section 2.3; 18.0 MΩ cm; H$_2$O-A) and with more stringent procedures (Section 2.3; H$_2$O-B); these artifacts are avoided here using H$_2$O subjected to more stringent degassing procedures, which are then used in all other experiments (H$_2$O-B; Section 2.3) reported in this study. HD formation rates were measured on Pt/γ-Al$_2$O$_3$ and on unsupported Pt powders before, during, and after exposure to H$_2$O-A or H$_2$O-B.

Figure 1 shows HD formation rates (normalized to the rates measured upon initial contact with reactants, $r_{HD,0}$) as a function of the time elapsed in contact with reactants by using (a) H$_2$O-A or (b) H$_2$O-B in the reactant mixtures. H$_2$–D$_2$ exchange rates were stable under anhydrous conditions (Figure 1a, $t < 6$ ks) but decreased upon contact with 20 kPa H$_2$O-A on both Pt/γ-Al$_2$O$_3$ and Pt powders (Figure 1a, 6–26 ks, as indicated by the shaded region) and ultimately reached constant values. Rates increased instantaneously when H$_2$O-A was removed from the inlet stream (26 ks, Figure 1a), but the rates were not restored to the initial values even after 20 ks (0.58 ± 0.03 and 0.52 ± 0.02 fractions of the initial rates on Pt/γ-Al$_2$O$_3$ and Pt powders, respectively); these irreversible titration effects are unrelated to the support effects, as demonstrated by the similar effects observed on both samples. They seem to reflect either the restructuring or titration of Pt nanoparticles, which cannot be reversed upon the removal of water at 473 K; any consequences of using water co reactants with different trace impurities would confirm the latter interpretation.

Figure 1b shows that HD formation rates decreased upon contact with H$_2$O-B (indicated by the shaded region), which, in contrast with the data in Figure 1a, are recovered to initial rates after removal of H$_2$O from the inlet stream. The concentration of any trace impurities removed by more extensive degassing (to prepare H$_2$O-B) cannot plausibly influence the extent of any restructuring. These data implicate impurities that can be removed from liquid H$_2$O by more stringent degassing as the origins of the lower rates and the incomplete restoring of initial rates when H$_2$O-A is used.

CO$_2$ dissolves in H$_2$O at appreciable concentrations upon contact with ambient air; it dissociates on Pt metal surfaces at near ambient temperatures to CO* and O* and also reacts with O* to form stable bidentate carbonates. O* is readily removed by H$_2$ at the typical temperatures of H$_2$–D$_2$ exchange (383–473 K), but CO* and carbonates desorb (and/or react with H$_2$) only at higher temperatures. Pt powders exposed to H$_2$O-A during exchange measurements (10 kPa H$_2$, 10 kPa D$_2$, 20 kPa H$_2$O, 20 ks, 473 K) were used for anhydrous exchange reactions with H$_2$–D$_2$ mixtures 10 kPa H$_2$ and 10 kPa D$_2$) as the reaction temperature was gradually increased to 823 K (at 0.033 K s$^{-1}$); exchange rates were fully restored when measured again at 473 K after such temperature cycling (Figure SI-2, Section SI-3.1). A similar temperature cycle with N$_2$ did not restore initial rates, apparently because of the dissociation of some CO* species or the formation of carbonate species before desorption or reaction (Figure SI-2, Section SI-3.1). Contact with CO$_2$ (0.4 kPa for 3.6 ks) similarly led to lower H$_2$–D$_2$ exchange rates (0.36 ± 0.02 times the initial rate) during its cofeed (Figure SI-3, Section 3.1); these rates recovered slightly after CO$_2$ was removed but reached asymptotic rates lower than those before exposure to CO$_2$ (0.44 ± 0.05 times the initial rate) after 3 ks, similar to the effects observed in the data shown in Figure 1a using H$_2$O-A. These data implicate dissolved CO$_2$ (through its surface reactions to form CO) as the trace contaminant in H$_2$O-A; the presence of such contaminants causes significant kinetic artifacts that, if unrecognized or eliminated, could be inaccurately interpreted as an effect of water on the binding of hydrogen adatoms; such artifacts remain consequential whether H$_2$O is present in its gaseous, bound, or liquid states. They can be avoided using the degassing procedure described in Section 2.3 and H$_2$O-B has been used in all experiments described below. These treatments may seem obvious in
3.2. Kinetic Trends and Analysis of Isotopic Exchange Rates on H$_2$O and D$_2$ Pressures. Forward turnover rates of H$_2$O–D$_2$ exchange are defined here as the (equal) rates of disappearance of D$_2$ and H$_2$O (which are also equal to the combined rates of HD and H$_2$ or HDO and D$_2$O formation, respectively). They were measured on Pt/$\gamma$-Al$_2$O$_3$ at 2–40 kPa H$_2$O-B (treated as described in Section 2.3), 2–80 kPa D$_2$, and 473 K. Exchange rates increased with increasing H$_2$O and D$_2$ pressures (sublinearly, Figure 2).

Several reaction channels were examined in order to assess their ability to account for these kinetic trends; these included some previously proposed routes involving reactions of (a) H$_2$O(g) with D*, (b) H$_2$O* with D**, (c) H$_2$O* with D' (H$_2$O* and D' are adsorbed at distinct noncompeting sites), and (d) H$_2$O dissociation (to form OH* and H*) and recombination of OH* and D* at (●) 2.5, (■) 5, (▲) 10, (▲) 20, and (◆) 40 kPa H$_2$O-B. Calculated rates were obtained by regressing the data to the function form of the rate equations associated with each pathway (details in Section 3).

Figure 3. Measured and calculated (from regressed rate parameters) H$_2$O–D$_2$ isotopic exchange rates on Pt/$\gamma$-Al$_2$O$_3$ at 473 K mediated by the reactions of (a) H$_2$O(g) and D*, (b) H$_2$O* and D**, (c) H$_2$O* with D' (H$_2$O* and D' are adsorbed at distinct noncompeting sites), and (d) H$_2$O dissociation (to form OH* and H*) and recombination of OH* and D* at (●) 2.5, (■) 5, (▲) 10, (▲) 20, and (◆) 40 kPa H$_2$O-B. Calculated rates were obtained by regressing the data to the function form of the rate equations associated with each pathway (details in Section 3). The rate constants and equilibrium constants in these equations were obtained by regressing all of the data in Figure 2 to the respective functional forms of the rate equations by minimizing the sum of the squares of relative deviations between measurements and model predictions; the results of these regressions are shown as parity plots in Figure 3. Figure 3 demonstrates that pathways (b–d) cannot accurately describe the measured rates. Moreover, the regressed value of the equilibrium constant ($K_3$) for D$_2$ dissociative adsorption

$$D_2 + 2^* \xrightarrow{K_3} 2D^*$$

in each of these pathways was very small (Tables SI-2–SI-4; <1.5 × 10$^{-12}$ kPa$^{-1}$) and would lead to Pt nanoparticle surfaces that remain essentially bare at the conditions of these measurements (fractional coverages <10$^{-5}$; 5–80 kPa D$_2$). Such low coverages stand in contrast with the saturated D* coverages observed under anhydrous conditions on 1.6 nm Pt particles under these conditions (2–80 kPa D$_2$ and 473 K) and even at higher temperatures. Pathway (a) was able to describe rate data modestly well; the large uncertainty in the regressed equilibrium constant for D$_2$ dissociative adsorption ($K_3 = 2.4 \times 10^{-14} \pm 24$ kPa$^{-1}$; eq 1) indicates that the model is relatively insensitive to the surface coverages of D adatoms. Thus, in order to visualize deviations in the experimental data from the model at expected D*
coverages, the data (Figure 2) were also regressed to the relevant rate equation for pathway (a) (eq SI-20 and Section SI-4) by setting the value of $k_1$ to that estimated (1.4 kPa$^{-1}$; 473 K) from the average enthalpy and entropy of adsorption ($-43$ kJ mol$^{-1}$ and $-50$ J mol$^{-1}$ K$^{-1}$) measured previously from H$_2$ dissociative chemisorption studies ($\Delta H_{222} = -40$ to $-46$ kJ mol$^{-1}$, 0.5 ML; $\Delta S_{222} = -20$ to $-80$ J mol$^{-1}$ K$^{-1}$, 0.2–1.0 ML), which shows thermodynamic isotope effects near unity.\(^\text{17}\) The resulting model descriptions show systematic deviations from the measured rates, as shown in Figure 4.

![Graph showing measured and calculated exchange rates](image)

**Figure 4.** Measured and calculated (from regressed rate parameters) H$_2$O–D$_2$ isotopic exchange rates on Pt/γ-Al$_2$O$_3$ at 473 K mediated by reactions of H$_2$O(g) and D$^\circ$ (pathway (a)) at (•) 2.5, (■) 5, (▲) 10, (◇) 20, and (○) 40 kPa H$_2$O-B. Calculated rates were obtained using a fixed value for $K_1$ (1.4 kPa$^{-1}$), estimated from prior chemisorption studies.\(^\text{18}\)

Pathways b–d were also examined using similar protocols (described in Section SI-4) and showed significantly larger deviations than those in Figure 3, as expected. These pathways (a–d) were therefore discarded and considered to be inconsistent with the combined chemisorption and exchange rate data.

### 3.3. H$_2$O–D$_2$ Isotopic Exchange Pathways on Pt/γ-Al$_2$O$_3$

H$_2$–D$_2$ exchange on surfaces saturated with H$^*$ and D$^*$ occurs via the dissociative adsorption of H$_2$ (or D$_2$) at spaces arising from the displacement of adatoms to alternate binding modes (e.g., atop vs fcc).\(^\text{37}\) H$_2$O may also adsorb on Pt surfaces, competing with hydrogen adatoms. Thus, another plausible H$_2$O–D$_2$ exchange pathway involves D$_2$ dissociation to D$^*$ (step 1.1, Scheme 1) and competitive adsorption with the H$_2$O$^*$ species formed in step 1.2 (Scheme 1). H$_2$O$^*$ can then desorb (step 1.3, Scheme 1) or exchange its H-atoms with D$_2$ molecules that bond via noncompetitive displacements of D$^*$, leading to the formation of HDO$^*$ and HD (step 1.5, Scheme 1). The desorption of HDO$^*$ (step 1.4, Scheme 1) then completes an isotopic exchange event, while additional exchange between HDO$^*$ and D$_2$ would ultimately form D$_2$O$^*$ (step 1.6, Scheme 1). As in H$_2$–D$_2$ exchange, the seemingly “direct” (i.e., Eley–Rideal) reactions of D$_2$(g) with H$_2$O$^*$ (steps 1.5 and 1.6, Scheme 1) are likely to involve a series of steps in which D$_2$ dissociates at vacancies that form via the local displacement of mobile D$^*$ species onto vicinal locations, where they assume alternate binding modes (atop vs fcc) within D$^*$–H$_2$O$^*$ adlayers, followed by fast exchange between these D$^*$ adatoms and H$_2$O$^*$; such routes can lead the kinetic impression of a direct reaction between a gaseous D$_2$ molecule and H$_2$O$^*$.

The steps and reversibility assumptions in Scheme 1 are used next to derive an equation for H$_2$O–D$_2$ exchange rates (defined as the rate of disappearance of H$_2$O or D$_2$ isotopolog: $r_{H,O,f}$ and $r_{D,O,f}$ using pseudo-steady-state formalisms for all bound species. The derivation includes kinetic isotopic effects for H$_2$O desorption (steps 1.2–1.4, Scheme 1) and for D$_2$ reactions with H$_2$O$^*$ (H$_2$O$^*$ and HDO$^*$) (steps 1.5–1.6, Scheme 1) near unity, an inference derived from independent H$_2$–D$_2$ isotopic exchange data (and by the similarity between the proposed TS for H$_2$O–D$_2$ exchange and H$_2$–D$_2$ exchange). Exchange rates derived using these protocols and assumptions are described by

$$
\frac{-\Delta D_{2,f}}{\theta_{D_{2,f}}} = -r_{H,O,f} = r_{D,O,f} + r_{D,O,f} = k_f(D_2O)(D_2) = \frac{k_f(D_2O)(D_2)}{(H_2O) + \frac{k_f}{k_e}((D_2))}(1 + \frac{k_e}{k_f}(D_2))
$$

where $k_f$ and $K_f$ are the rate and equilibrium constants for step i in Scheme 1 (derivation details in SI-5.1). The three parameters ($k_6$, $\frac{K_6}{K_5}$, and $k_{3,i}$; eq 2) were estimated regressing all rate data (Figure 2) to the functional form of eq 2. Their values are $121 \pm 8$ kPa$^{-1}$ s$^{-1}$, $2.1 \pm 0.3$ kPa$^2$, and $(4.0 \pm 2.4) \times 10^8$ s$^{-1}$, respectively. A sensitivity analysis to determine of how each parameter accounts for the regression uncertainties (shown in Section SI-6) shows that $k_6$, $\frac{K_6}{K_5}$, and $k_{3,i}$ can all be determined with certainty from these data. Figure 5 shows the excellent agreement for the measured H$_2$O–D$_2$ exchange rates (over a 100-fold range) and those predicted from eq 2 and the value of its regressed parameters. The $\frac{K_f}{K_i}$ term represents the ratio of equilibrium constants for $D_2$ dissociative adsorption and H$_2$O molecular adsorption and leads to $\frac{\theta_{D_{2,f}}}{\theta_{H_{2,O,f}}}$ estimates between 0.13 and 34 for the H$_2$O and D$_2$ pressure ranges (2–40 kPa H$_2$O and 2–80 kPa D$_2$) used here (Figure 2); these relative coverages are given by

$$
\frac{\theta_{D_2}}{\theta_{H_2O}} = \frac{\frac{K_5}{K_6}(D_2)}{K_3(H_2O)}
$$

These values of $\frac{\theta_{D_{2,f}}}{\theta_{H_{2,O,f}}}$ indicate that D$^*$ and H$_2$O$^*$ coverages are both kinetically consequential at the conditions used to measure the exchange rates shown in Figure 2 (2–40 kPa H$_2$O and 2–80 kPa D$_2$, 473 K). The presence of H$_2$O$^*$ at consequential coverages seems at odds with its propensity to desorb readily from Pt surfaces at low temperatures (~200 K).\(^\text{65,66}\) Yet, H$_2$O adsorption enthalpies on Pt(111) surfaces ($\sim51.3 \pm 1.6$ kJ mol$^{-1}$, 0.5 ML H$_2$O)\(^\text{67,68}\) are similar in magnitude to those for dissociative H$_2$ adsorption (~40 to ~46 kJ mol$^{-1}$, 0.5 ML, 1.6 nm Pt particles).\(^\text{69}\) The temperatures (~400 K) required for the desorption of H$^*$ (or D$^*$) from Pt surfaces may reflect higher energy barriers and smaller entropy loss (due to the mobility of H$^*$ adatoms) associated with the recombination of H$^*$/$D^*$ adatoms compared to the molecular desorption of H$_2$O. Equation 2 and its mechanistic under-
pinnings accurately account for all measured kinetic trends in \( \text{H}_2\text{O} - \text{D}_2 \) exchange rates; they are also consistent with the saturation coverages of hydrogen adatoms reported in earlier studies at pressures and temperatures similar to those used to measure exchange rates.\(^{18,37} \)

This contrasts with the inaccurate descriptions of measured exchange rates based on alternate mechanisms proposed in previous studies (pathways (a–d); Section 3.2).

### 3.4. Consequences of Bound \( \text{H}_2\text{O} \) Molecules as Reactive Intermediates in \( \text{H}_2\text{O} - \text{D}_2 \) Exchange

\( \text{H}_2\text{O}^* \) adsorbs competitively with \( \text{D}^* \) (and \( \text{H}^* \)) at kinetically detectable coverages (eq 3) and acts as a reactive intermediate that forms not only \( \text{HDO}^* \) (step 1.5, Scheme 1) but also \( \text{D}_2\text{O}^* \) (step 1.6, Scheme 1) as primary products (in a single surface sojourn) via sequential \( \text{D}_2 \) reactions, without requiring the intervening desorption and readsoption of \( \text{HDO} \). These steps stand in contrast with alternate routes that do not involve bound \( \text{H}_2\text{O} \) molecules as direct reactive species (e.g., \( \text{H}_2\text{O}(g) + \text{D}^* \), pathway (a) in Section 3.2);\(^{34} \) these alternate routes can form \( \text{D}_2\text{O} \) only through subsequent readsoption of gaseous \( \text{HDO} \) but not in a single surface sojourn. \( \text{D}_2\text{O} \) formation rates (and the ratio of \( \text{D}_2\text{O} / \text{HDO} \)) extrapolated to zero residence time are thus expected to be nonzero if exchange occurred via the pathways described in Scheme 1.

Figure 6 shows \( \text{D}_2\text{O} / \text{HDO} \) ratios at different bed residence times (20 kPa \( \text{H}_2\text{O} \), 20 kPa \( \text{D}_2 \), and 473 K) on Pt powders; the asymptotic ratio is 0.056 ± 0.002 (Figure 6). This ratio reflects the relative rates of \( \text{D}_2\text{O}^* \) and \( \text{HDO}^* \) desorption as primary products (steps 1.3 and 1.4, Scheme 1) and, in turn, their relative coverages on Pt surfaces (in the absence of significant kinetic and thermodynamic isotope effects). This nonzero value, indicative of the ability of \( \text{D}_2\text{O} \) to form in a single surface sojourn, provides compelling evidence for kinetically competent bound \( \text{H}_2\text{O} \) species as intermediates in \( \text{D}_2 - \text{H}_2\text{O} \).
exchange. The asymptotic ratio predicted by the reaction channel depicted in Scheme 1 is (derivation in Section SI-5.2)

$$\frac{r_{D_2O}}{r_{HDO}} = \frac{k_d(D_2)}{2k_s}$$

(4)

The regressed values of $k_d$ (121 ± 9 kPa$^{-1}$ s$^{-1}$) and $k_s$ ((4.0 ± 2.4) × 10$^4$ s$^{-1}$), obtained independently from the regression of exchange rate data in Figure 2 to the functional form of eq 2, and the $D_2$ pressure used in the residence time experiments (20 kPa) give an asymptotic $D_2O/HDO$ ratio of 0.061 ± 0.037, in excellent agreement with the measured values (0.056 ± 0.002; Figure 6). These results are consistent with the mechanistic underpinnings provided by the steps in Scheme 1; they contradict the predictions from alternate pathways that do not involve bound $H_2O^*$ at the surfaces as mediators of exchange turnovers (e.g., pathway (a); Section 3.2).

3.5. Effects of Pt Nanoparticle Size on $H_2O$–$D_2$ Exchange Activation Barriers. $H_2O$–$D_2$ exchange rates (5 kPa $H_2O$–$B$, 40 kPa $D_2$) were measured at different temperatures (423–1073 K) on Pt/γ-Al$_2$O$_3$ and Pt powders in order to estimate the activation energies (Figure 7). Differences in activation energy are expected when the rate of a given reaction is sensitive to Pt surface coordination and thus nanoparticle size$^{70–72}$. The apparent activation barriers measured on Pt/γ-Al$_2$O$_3$ (1.9 nm mean diameter) and Pt powders (400 nm) for temperatures between 423 and 900 K were similar and within experimental uncertainties (15.6 ± 0.1 kJ mol$^{-1}$ and 15.3 ± 0.1 mol$^{-1}$, respectively), indicating that $H_2O$–$D_2$ isotopic exchange rates are not sensitive to the Pt nanoparticle size.$^4$

These activation barriers reflect the combined temperature effects of $k_d$ and $k_s$ (eq 2), each with their expected exponential dependences. These combined functional forms, however, do not, in general, lead to a simple exponential dependence for exchange rates described by eq 2; yet, linear trends (on a semilog scale) are evident in Figure 7 for temperatures between 423 and 900 K, suggesting that eq 2 assumes a simpler form throughout this range of temperatures and pressures (40 kPa $D_2$, 5 kPa $H_2O$). The value of $\frac{k_d}{k_s}(D_2)$

(0.12 ± 0.074; 473 K) is much smaller than unity, and the $H_2O$ pressure term ($H_2O = 5$ kPa) is small compared to $\frac{\sqrt{K_3}}{K_2}\sqrt{(D_2)}$ (13 ± 3 kPa; 473 K), leading to an approximate form of eq 2

$$-\eta_{H_2O} = r_{HDO} + r_{D_2O} = \frac{k_dK_s}{K_2}\sqrt{(H_2O)}\sqrt{(D_2)}$$

(5)

Therefore, the measured activation barriers (15.6 ± 0.1 kJ; 423–900 K; Pt/γ-Al$_2$O$_3$) predominantly reflect the temperature dependence of the $\frac{k_d}{k_s}$ term (eq 5), thus preserving the strictly exponential trends evident from the date shown in Figure 7.

Above 900 K, exchange rates increase more sensitively with temperature (Figure 7), and the larger apparent barrier (40 ± 0.4 kJ; Pt/γ-Al$_2$O$_3$) reflects the emerging contributions from other elementary steps to measured rates.$^8,69$ This barrier was estimated by extrapolating the rate contributions from low-temperature channels ($D_2$–$H_2O^*$ and $D_2$–$HDO^*$, steps 1.5–1.6, Scheme 1; 423–873 K) and subtracting them from the exchange rates measured at high temperatures (>900 K). This difference was regressed to an Arrhenius functional form to obtain the barrier for these high-temperature channels (87 ± 8 kJ mol$^{-1}$); these higher values may reflect, in part, contributions from dissociation–recombination routes that contribute to exchange rates, as surfaces become less densely covered at higher temperatures.$^{37}$

$H_2O$ dissociation occurs during water–gas shift reactions on Pt-based catalysts above 500 K.$^{82–64}$ $H_2O$–$D_2$ exchange may also occur via $H_2O$ dissociation at these higher temperatures to form $OH^*$ and $H^*$ and then $HDO$ via $OH^*$–$D^*$ recombination. The exchange rates as the coverage of bound species decreases with increasing temperature (>900 K)$^{18,69}$ are then given by

$$r = k_{di}H_2O(H_2O)$$

(6)

(derivation in Section SI-4.4.2). In this case, the $k_{di}$ parameter is the rate constant for $H_2O^*$ dissociation, and $K_{H_2O}$ is the
equilibrium constant for molecular H₂O adsorption. The measured barriers at high temperatures (87 ± 8 kJ mol⁻¹) may therefore reflect the temperature effects on $k_w K_{\text{H}_2\text{O}}$ which represent, in turn, the energy required to dissociate H₂O on Pt surfaces from a gaseous H₂O molecule; this value resembles those reported for H₂O dissociation on Pt surfaces (Pt(100): 61 kJ mol⁻¹ and Pt(111): 75 kJ mol⁻¹ at 463 K), suggesting that H₂O–D₂ exchange on Pt occurs via dissociative routes as surfaces become less densely covered at these higher temperatures. These processes become favored over those prevalent on densely covered surfaces at low temperatures; the latter exploit instead the mobility of bound species that become weakly bound at high coverages to avoid the energy penalties imposed by the need to create surface vacancies through recombinative desorption events. These low-temperature routes are mediated by dissociation events of H₂O and D₂ at “spaces” that form locally and momentarily within the dense mobile adlayers that prevail at these low temperatures. Such interpretations are similar to those previously proposed for the evolution of H₂–D₂ isotopic exchange channels with increasing temperature (>900 K).³⁷

3.6. H₂–D₂ and H₂O–D₂ Exchange Rates in H₂O–H₂–D₂ Mixtures on Pt/y-Al₂O₃. H₂–D₂ exchange occurs predominantly via H₂–D* (and D₂–H*) associative reactions on Pt nanoparticles at temperatures below 700 K under anhydrous conditions; these reaction routes are not expected to change when gaseous (H₂O(g)) or bound (H₂O*) water is also present in the fluid or adlayer phases, respectively. The addition of H₂ to H₂O–D₂ mixtures introduces the additional elementary steps depicted in the second section of Scheme 1. These additional steps include HDO* and D₂O* reactions with H₂ to form H₂O* (step 1.11, Scheme 1) and HDO* (step 1.12, Scheme 1) (and HD), respectively, as well as those required for H₂–D₂ exchange (steps 1.7–1.10, Scheme 1). Consequently, the rates of HD formation reflect the combined contributions from H₂–D₂ and H₂O–D₂–H₂ exchange in H₂O–H₂–D₂ mixtures. The proposed elementary steps for the specific H₂–D₂ exchange processes and the kinetic treatment that accurately describes the measured H₂/D₂ exchange were reported previously;³⁷ they are directly applicable to the description of expressions for H₂–D₂ and H₂O–D₂ isotopic exchange rates when using H₂O–H₂–D₂ reactant mixtures.

H₂O–H₂–D₂ mixtures form HD molecules through both H₂O–D₂ and H₂–D₂ exchange, leading to HD formation (r_{HD}) and H₂O consumption (−r_{H₂O}) rates (at conditions far from isotopic equilibrium; derivation details in Section S1.5.3) given by

$$r_{HD} = r_{H_2-D_2} + r_{H_2O-D_2}$$

$$= \frac{2k_i \sqrt{\gamma_{\text{H}_2}}}{K_i} \frac{(\text{H}_2)(\text{D}_2)}{\sqrt{(\text{H}_2) + (\text{D}_2)}} \left(1 + \frac{k_w}{K_w} (\text{D}_2)\right) + k_b (\text{H}_2\text{O})(\text{D}_2)$$

$$= \left(\frac{(\text{H}_2\text{O}) + \frac{2k_i^b}{K_i} \sqrt{(\text{H}_2) + (\text{D}_2)}}{(\text{H}_2) + (\text{D}_2)}\right) \left(1 + \frac{k_w}{K_w} (\text{D}_2)\right)$$

where k_i and K_i correspond to the parameters for each elementary step i in Scheme 1. These equations were obtained for the specific case (applicable here) when exchange rates between water and dihydrogen (steps 1.5–1.6 and 1.11–1.12, Scheme 1; $k_b$) are much smaller than water desorption rates (reverse of steps 1.2–1.4, Scheme 1; $k_{w^{-1}}$). This case is evidenced in this study by the small values of $\frac{k_b}{k_{w^{-1}}}$ (0.015–0.06, dimensionless; 10–40 kPa D₂); the value of $\frac{k_b}{k_{w^{-1}}}$ ((3.0 ± 1.8) × 10⁻³ kPa⁻¹) was regressed previously from H₂O–D₂ exchange data (Section 3.2) obtained under conditions that allow for its measurement (2.5–40 kPa H₂O, 5–80 kPa D₂).

The rate of HD formation is given by the sum of H₂O–D₂ and H₂–D₂ exchange pathways (eq 7). The rate of H₂–D₂ exchange can therefore be obtained by subtracting eq 8 from 7 and simplifying to obtain

Figure 8. Parity plots of (a) H₂O–D₂ (eq 8) and (b) H₂–D₂ (eq 9) exchange rates in H₂–D₂–H₂O mixtures at (■) 5, (▲) 10, and (◆) 20 kPa of H₂O (H₂O–B) on Pt/y-Al₂O₃ (473 K). Rates are predicted using kinetic and thermodynamic parameters regressed from independent H₂–D₂ and H₂O–D₂ (Section 3.2) isotopic exchange experiments. The additional scatter in H₂–D₂ exchange data is attributed to its calculation through the subtraction of H₂O–D₂ exchange rates from the overall HD formation rates (eq 9).

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\[ r_{H_2-D_2} = r_{H_D} + r_{H_2O-D_2} = \frac{2k_4 \frac{\sqrt{k_3}}{k_1} (H_2)(D_2)}{(H_2O) + \frac{2\sqrt{k_3}}{k_1} (H_2) + (D_2)} \]  

Equations 7–9 (and the elementary steps in the second section of Scheme 1 for \( H_2O-H_2-D_2 \) exchange) require only one parameter \( k_d \) in addition to those already derived from the exchange rates measured with \( H_2O-D_2 \) mixtures \( (k_6, \frac{\sqrt{k_3}}{k_1}, \text{and } k_{3,4}) \) Section 3.2). This parameter \( k_d \) is the rate constant for \( H_2-D_2 \) exchange via \( H_2 \) reactions with \( D^* \) or \( D_2 \) reactions with \( H^* \) (steps 1.9–1.10, Scheme 1); it is identical for steps 1.9 and 1.10 because these reactions exhibit no detectable kinetic isotope effects. The \( k_d \) value was calculated from \( H_2-D_2 \) exchange rates measured on this Pt/\( \gamma \)-Al\(_{2}O\(_{3}\) sample under anhydrous conditions \((118 \pm 6 \text{ kPa}^{-1} \text{ s}^{-1}) \) at 473 K (initial rates in Figure S1-3 and Section S1-3); this value can be used here, together with those of the parameters measured in Section 3.2 \((k_6 = 121 \pm 7 \text{ kPa}^{-1} \text{ s}^{-1}, \frac{\sqrt{k_3}}{k_1} = 2.1 \pm 0.4 \text{ kPa}^0.5\), \( k_{3,4} = \left((4.0 \pm 2.4) \times 10^4 \text{ s}^{-1}\right)\), to describe \( H_2O-D_2 \) (eq 8) and \( H_2-D_2 \) (eq 9) exchange rates for \( H_2O-H_2-D_2 \) mixtures \((473 \text{ K})\) if Scheme 1 is applicable for such mixtures without any need to vary the three parameters previously measured in independent experiments. The resulting descriptions do not require the refinement of any additional parameters.

\( H_2-D_2 \) and \( H_2O-D_2 \) exchange rates were measured on Pt/\( \gamma \)-Al\(_{2}O\(_{3}\) at 473 K and a broad range of \( H_2O \) pressures \((5-20 \text{ kPa}; \text{ H}_2O-\text{B}, \text{ H}_2 \text{ (5-20 kPa), and D}_2 \text{ (10-40 kPa) pressures (rate data in Table S1-2 and Section S1-7). The } \)parity plots in Figure 8 show that eqs 8 and 9 accurately describe the rates of \( H_2-D_2 \) and \( H_2O-D_2 \) isotopic exchange in ternary \( H_2O-H_2-D_2 \) mixtures without any changes in the elementary steps described in Scheme 1 or in the previously determined magnitudes of their relevant parameters. The proposed kinetic model for \( H_2O-D_2 \) isotopic exchange (Scheme 1, first half) brings together the extensive exchange rate data set in earlier sections with the demonstrated mechanism and measured rate parameters for \( H_2-D_2 \) exchange under anhydrous conditions \( (\text{Scheme 1, second half})\); these two sets of elementary steps occur in parallel but, in contrast with the earlier studies, \( (\text{Figure 9})\), on surfaces that contain kinetically detectable coverages of both \( H^*/D^* \) and \( H_2O^* \) in the case of \( H_2O-H_2-D_2 \) mixtures.

3.7. Consequences of Intrapore Liquid Water on HD Formation Rates in \( H_2O-H_2-D_2 \) Mixtures. The mechanistic framework developed in the previous sections forms the foundation for probing the effects of liquid water on \( H_2-D_2 \) and \( H_2O-D_2 \) isotopic exchange rates. The results described in this section demonstrate that capillary effects that lead to the formation of a \( H_2O \) liquid phase within \( \gamma \)-Al\(_{2}O\(_{3}\) mesopores that contain Pt nanoparticles do not lead to different exchange channels or to \( H_2O-H_2-D_2 \) exchange rates and kinetic parameters that differ detectably from those in contact with \( H_2O \) pressures that do not lead to capillary condensation of a liquid phase.

The individual rates of \( H_2O-D_2 \) and \( H_2-D_2 \) isotopic exchange (defined as \( r_{H_2O-D_2} = -r_{H_2O} \) and \( r_{H_2-D_2} = r_{H_D} - r_{H_2O-D_2} \) respectively) using \( H_2-D_2-H_2O \) mixtures were measured on Pt/\( \gamma \)-Al\(_{2}O\(_{3}\) under conditions that cause the condensation of \( H_2O \) \((323 \text{ K})\) as \( H_2O-B \) treated as described in Section 2.3) pressure increases \((\text{Figure 9); 20 kPa H}_2 \text{ and 20 kPa D}_2 \). The \( H_2O \) pressure is expressed here as a relative pressure ratio \((P/P^0; P^0 = 12.3 \text{ kPa})\). Figure 9 also depicts the fraction of the \( \gamma \)-Al\(_{2}O\(_{3}\) area \( \text{(and therefore of Pt nanoparticles that reside on such surfaces) that resides within liquid-filled pores as a function of the relative H}_2O \) pressure \( (\text{Section S1-2}), \) estimated from \( H_2O \) uptakes and pore filling calculated using the procedures described in Section 2.4 and in previous studies. These estimated \( H_2O \) uptake values increase sharply at relative pressures above 0.6–0.7 \((\text{Figure 9})\), indicative of the incipient formation of a \( H_2O \) liquid phase within \( \gamma \)-Al\(_{2}O\(_{3}\) voids that are distributed in effective diameter. The condensation of water at similar relative pressures has been demonstrated previously using IR studies at lower temperatures \((296 \text{ K})\). The secondary (top) abscissa in Figure 9 shows the mean number of \( H_2O \) monolayers at the \( \gamma \)-Al\(_{2}O\(_{3}\) surfaces, calculated using the molar volume and surface tension properties of \( H_2O \) and the specific surface area of \( \gamma \)-Al\(_{2}O\(_{3}\).

The data in Figure 9 show that \( H_2-D_2 \) exchange rates decrease and \( H_2O-D_2 \) exchange rates increase monotonically (and to a similar extent) with increasing \( H_2O \) pressure, without any detectable shift in their kinetics, as the physical state of \( H_2O \) evolves from gaseous to physiosorbed adlayers to a liquid phase. The solid lines in Figure 9 represent the rates predicted by eqs 8 and 9 using regressed values for \( k_6, \frac{\sqrt{k_3}}{k_1}, k_{3,4}, \) and \( k_d \) \((1.6 \pm 0.1 \text{ kPa}^{-1} \text{ s}^{-1}, 1.1 \pm 0.1 \text{ kPa}^0.5, (1.6 \pm 5.1) \times 10^5, \) and \( 1.9 \pm 0.2 \text{ kPa}^{-1} \text{ s}^{-1}\)) respectively. Figure 9 shows that the kinetic model derived previously for strictly gaseous reactant mixtures \( (\text{eq 8-9})\) with a single value for each parameter \( (k_6, \frac{\sqrt{k_3}}{k_1}, k_{3,4}, \text{and } k_d) \) is able to describe rates in the absence or presence of an intrapore liquid phase. These values cannot be compared numerically to those reported above \((\text{Section 3.3; 473 K})\) because of the lower temperatures \((323 \text{ K})\) required to enable the formation of liquid \( H_2O \) at ambient reactor pressures; nevertheless, the agreement obtained with param-
Scheme 2. Thermodynamic Cycle Showing $\text{H}_2$–$\text{D}_2$ Exchange (and Its Relevant TS) in the Absence (Top) and Presence (Bottom) of Liquid $\text{H}_2\text{O}$

\[ \frac{r_{(aq)}}{r_{(g)}} = \frac{k_{(aq)}}{k_{(g)}} = \frac{a_{(aq)}^{i}}{a_{(g)}^{i}} = \frac{r_{(aq)}^{E}}{r_{(aq)}^{E}} = e^{-\Delta G^{i}/RT} \]  \tag{11} \]

where $\Delta \Delta G^{i}$ is the difference in Gibbs free energy of activation (referenced to gaseous reactants) between the reaction in the aqueous phase and that in the gas phase

\[ \Delta \Delta G^{i} = \Delta G_{(aq)}^{E} - \Delta G_{(g)}^{E} = \left( G_{TS,(aq)}^{E} - G_{TS,ideal}^{E} - G_{\text{reactants}}^{E} \right) - \left( G_{TS,(g)}^{E} - G_{TS,ideal}^{E} - G_{\text{reactants}}^{E} \right) \]  \tag{12} \]

where $G^{E}$ represents the excess Gibbs free energy. Eqs 11 and 12 show that differences in rates arising from the presence of a contacting dense phase reflect the differences in the Gibbs free energy.
Scheme 3. Reaction Coordinate Diagram for H\textsubscript{2}−D\textsubscript{2} Exchange on Pt when the Contacting Fluid Phase is Gaseous (Dashed Black Lines) and when It is Liquid Water (Dotted Blue Lines)

The dashed black pathway in Scheme 3 depicts the reaction energy of activation $\Delta G^\dagger$, specifically the excess free energy of the TS ($G_{TS(aq)} - G_{TS(g)}^E = RT\ln(y_{H^2(g)}^1) - RT\ln(y_{D^2(g)}^1)$) (13).

These concepts are next used to interpret the absence of consequences of liquid water on H\textsubscript{2}−D\textsubscript{2} and H\textsubscript{2}O−D\textsubscript{2} isotopic exchange rates in H\textsubscript{2}−D\textsubscript{2}−H\textsubscript{2}O mixtures (Figure 9).

Our previous study demonstrated that H\textsubscript{2}−D\textsubscript{2} exchange channels on Pt surfaces saturated with H*/D* adlayers involve the dissociative adsorption of H\textsubscript{2} (or D\textsubscript{2}) at “landing” spaces made available by the local displacements of mobile H* or D* adatoms (atop) to alternate (fcc) binding sites on the Pt surface (denoted as ')\textsuperscript{37}

$$D_2 + H^* + k_1 H^* + D^* + D'$$ (14)

This elementary step (and its TS; Scheme 2 (top)) also describes events in which H\textsubscript{2} exchanges with D* with similar rates in eq 14 because of negligible kinetic isotope effects.\textsuperscript{37}

The dashed black pathway in Scheme 3 depicts the reaction coordinate diagram for this reaction with purely gaseous reactants; the rate constant $k_5(aq)$ reflects the difference in Gibbs free energy between the TS and the reactants (H\textsubscript{2}(g), D\textsuperscript{*}(g), and ')\textsuperscript{37}(aq)) in the absence of a solvating liquid (denoted by $\Delta G^\dagger_{(aq)}$; Scheme 3, dashed black pathway).

The data shown in Figure 9 indicate that H\textsubscript{2}−D\textsubscript{2} isotopic exchange is mediated by the same TS (Scheme 2 (bottom) and Scheme 3 (dotted blue lines)), albeit one being possibly different in stability, whether an aqueous liquid phase is present or not. The rate constant for the reaction in the presence of the liquid phase ($k_5(aq)$; Scheme 2 (bottom)) reflects the free energy of activation for the surface-bound TS in contact with liquid water ($\Delta G_{(aq)}^\dagger$; Scheme 3 (dotted blue lines)). The dissolution of gaseous species in liquid H\textsubscript{2}O is quasi-equilibrated under conditions of vapor−liquid equilibrium. The H* and D* coverages are set by quasi-equilibrated dissociative adsorption of H\textsubscript{2} and D\textsubscript{2}\textsuperscript{37} leading to equilibration among gaseous reactants, solvated reactants, and their respective bound species (denoted by red equilibrium reaction arrows, $\Rightarrow$, in Scheme 2). Schemes 2 and 3, taken together, consider that (in the absence of diffusional restrictions, leading to local chemical potential gradients) $\Delta G^\dagger$ values merely reflect the effects of the solvent on the excess free energy (or activity coefficient) of the TS (eqs 12 and 13). In the absence of such solvating effects, $\Delta G^\dagger$ is zero (eq 12), and $y_{H^2(g)}^1$ and $y_{D^2(g)}^1$ are identical (eq 13), thus precluding any consequence of liquid water on isotopic exchange rates. These concepts, illustrated here for H\textsubscript{2}−D\textsubscript{2} exchange reactions, also apply to H\textsubscript{2}O−D\textsubscript{2} exchange

$$D_2 + H_2O^{a^*} + k_5 H_2O^{a^*} + D^* + D'$$ (15)

and the relevant rate parameters for the unsolvated ($k_5(aq)$) and solvated ($k_5(aq)$) systems.

H\textsubscript{2}−D\textsubscript{2} exchange rates in the presence of H\textsubscript{2}O(g) are accurately described by eq 9 (Section 3.4); this equation accounts for competitive adsorption of H\textsubscript{2}O\textsuperscript{*} (step 1.2, Scheme 1) on Pt surfaces, whether such surfaces are in contact with liquid water or not. Rates of H\textsubscript{2}−D\textsubscript{2} exchange reactions in the aqueous phase (assuming the same reaction pathway as in the absence of a liquid phase; Schemes 2 and 3) are described by

$$r_{H_2→D_2} = \frac{2k_5(aq)\sqrt{K_{H_2(aq)}}}{k_{H_2(aq)}} \frac{(H_2)(D_2)}{\sqrt{(H_2) + (D_2)}}$$ (16)

The (aq) subscript in this equation denotes equilibrium and rate constants when liquid water is present. Similarly, H\textsubscript{2}O−D\textsubscript{2} exchange rates in gas-phase H\textsubscript{2}−D\textsubscript{2}−H\textsubscript{2}O mixtures are described by eq 8, while rates in the presence of liquid H\textsubscript{2}O are given by

\begin{align*}
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\end{align*}


\[ r_{\text{H}_2\text{O} - \text{D}_2} = -r_{\text{H}_2\text{O}} = \frac{k_{(a)}(\text{H}_2\text{O})(D_2)}{(\text{H}_2\text{O}) + \sqrt{\frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}}} \sqrt{(H_2) + (D_2)}} \left(1 + \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}(D_2)} \right) \]

(17)

It is evident when comparing eqs 16 and 17 to 9 and 8, respectively, that three rate constant ratios \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \), \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \), and one equilibrium constant ratio \( \frac{K_{(a)}(\text{H}_2\text{O})}{K_{(c)}} \) may plausibly differ from unity, reflecting changes in activity coefficients (eq 11) and thus informing about the consequences of a liquid H2O outer sphere on the surface-mediated exchange process of interest in this study.

The value of \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) reflects differences in the excess free energy \( \Delta \Delta G^\text{f} \); eqs 11 and 12 and activity coefficients (\( \gamma^\text{f} \); eq 13) of the TS for H2−D2 exchange in the presence and absence of a liquid, referenced to the gaseous reactants. These TSs are identical, except for possible interactions between the incoming H2 (or D2) molecule and the surrounding liquid. H2(g) is only weakly solvated by liquid water (\( \Delta H_{\text{diss}} = -3.2 \text{ kJ} \text{ mol}^{-1} \); 273–303 K), the effects of liquid water on H2 in the TS are also, therefore, expected to be weak. Our previous study also showed that this TS interacts with Pt surfaces through each of its three hydrogen atoms and closely resembles the bound intermediate (D* + H’ + D’; Scheme 3).37 The “late” TS thus exhibits nearly complete bonds with the surface and differs from other reactions for which the effects of liquids have been observed;55,66,76 these latter reactions exhibited “early” or “late” structures for entry and exit steps, respectively, and thus less complete bonds with the catalyst surface at their respective TSs, allowing for more interactions with the outer-sphere environment. The TS for H2−D2 exchange is thus expected to be stabilized primarily by interactions with the Pt surfaces and weakly influenced by the presence of liquid H2O, resulting in nearly identical activity coefficients (\( \gamma^\text{f} \) vs \( \gamma^\text{f} \); eq 13) and a \( \Delta \Delta G^\text{f} \) value near zero (eqs 12 and 13). This absence of solvation effects leads to a \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) ratio near unity (eq 12). The parameter \( k_3 \) is the rate constant for the reaction between D2 and H2O* (steps 1.5 and 1.6, Scheme 1). This elementary step is proposed to proceed via a nearly identical TS as for the reaction of D2 and H* (eq 14), making the arguments for the effects of liquid water on \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) and \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) ratios identical.

The \( \frac{k_{(a)}}{k_{(c)}} \) (and \( \frac{k_{(a)}}{k_{(c)}} \)) terms represent the ratios of equilibrium constants for H2 (or D2) dissociative chemisorption (\( K_3 \)) and H2O molecular adsorption (\( K_4 \)). These equilibrium constants can be defined rigorously using the thermodynamic activities of all species involved

\[ K_3 = \frac{a_{\text{H}_2}}{a_{\text{H}} a_{\text{H}}^*} \]

(18)

\[ K_4 = \frac{a_{\text{H}_2\text{O}^*}}{a_{\text{H}_2\text{O}} a_{\text{H}}^*} \]

(19)

As discussed above, all species in their gaseous (unsolvated) state (\( \text{H}_2(g), \text{D}_2(g), \text{H}_2^*(g), \text{D}_2^*(g), \text{H}_2\text{O}^*(g), \text{and} \text{ H}_2^*(g) \) is in equilibrium with their solvated counterparts (\( \text{H}_2(\text{aq}), \text{D}_2(\text{aq}), \text{H}_2^*(\text{aq}), \text{D}_2^*(\text{aq}), \text{H}_2\text{O}^*(\text{aq}), \text{and} \text{ H}_2^*(\text{aq}) \)); consequently, their chemical potentials and thermodynamic activities are identical in their two states to the extent that these intermediates are stabilized by direct coordination with the binding site (inner sphere). Molecularly bound H2O* is plausibly stabilized by the presence of liquid water. Several studies have shown, however, that adsorbed water on Pt(111) exhibits surprising “hydrophobic” qualities and only weak hydrogen-bonding interactions (<6 kJ mol\(^{-1}\)) compared to interactions with the surface (−51.3 ± 1.6 kJ mol\(^{-1}\), 0.5 ML H2O).55,66 \( K_3 \) and \( K_4 \) values are therefore expected to be only weakly affected by the nature or density of the contacting fluid phase, leading to \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) ratios near unity.

The \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) ratio reflects the difference in excess Gibbs free energy of the TS (eqs 11 and 12) for the desorption of water molecules (steps 1.2−1.4, Scheme 1) between Pt nanoparticles in contact with a liquid and those in contact with gaseous phases. It is this ratio that may seem most plausibly different from unity because H2O molecules in the dense liquid phase can make more H-bonding “contacts” with surface H2O molecules and with their desorption TS.\(^{85,86} \) Such dense protic environments could stabilize the desorption TS (steps 1.2−1.4, Scheme 1; an exit step) and increase desorption rates (leading to \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} > 1 \); eqs 11 and 12), and to a smaller \( \frac{k_{(a)}(\text{H}_2\text{O})}{k_{(c)}} \) value (eq 17), when liquid water is present. The regressed values of the \( \frac{k_{(a)}(\text{D}_2)}{k_{(c)}} \) term in eq 8 are, however, much smaller than unity and weakly influence the measured rates, even in the absence of a liquid phase (0.12 ± 0.074, Section 3.2). Its even smaller value when a liquid is present would make its contribution to the measured H2O−D2 exchange rates less consequential.

These inferences about the relevant ratios of rate and equilibrium constants \( \frac{k_{(a)(\text{H}_2\text{O})}}{k_{(c)}} \), \( \frac{k_{(a)(\text{H}_2\text{O})}}{k_{(c)}} \), \( \frac{k_{(a)(\text{H}_2\text{O})}}{k_{(c)}} \), \( \frac{k_{(a)(\text{H}_2\text{O})}}{k_{(c)}} \), and \( \frac{k_{(a)(\text{H}_2\text{O})}}{k_{(c)}} \) and the absence of detectable consequences of solvation for H2−D2 and H2O−D2 exchange rates are supported by our experimental data (Figure 9) and our mechanistic framework for their analysis. The formation of a H2O liquid phase within Pt/γ-Al2O3 mesopores does not detectably influence exchange rates, kinetic trends, or rate and equilibrium constants, which remain the same as those on nanoparticles in contact with a strictly gaseous phase. These findings show that the effects of liquid H2O on H2−D2 and H2O−D2 exchange are too weak to be detected experimentally, in contrast with other reactions for which such effects are reported (e.g., CH4 activation and polyl reforming).\(^{54,87,88} \) They also challenge the conclusions of previous studies\(^{14} \) that attribute the consequences of a liquid water phase for H2−D2 exchange rates to significant changes in the electronic properties of metals placed in contact with liquid water.\(^{54,55,33,55,64} \) Our study demonstrates that (1) the mechanism of exchange is unaffected by the physical form of water (gas or liquid) in contact with the catalyst (only the chemical potential of H2O influences rates—it is identical when the gas and liquid phases are in equilibrium), (2) the TSs for H2−D2 exchange on densely covered surfaces in contact with gas phase or liquid H2O are in equilibrium with one another, (3) H2−D2 (and H2O−D2) exchange rates are not
able to detect any preferential (de)stabilization of H* and D* intermediates because they report only the free-energy barrier between the TS and a densely covered surface in the gas phase (Scheme 3), and (4) H2−D2 (and H2O−D2) exchange rates do not detect changes in the combined effects of liquid H2O on the binding of the TS (inner sphere) nor its solvation (outer sphere).

The present study remains silent about the binding of reactive intermediates (e.g., H*, D*, and H2O*) and their respective adsorption equilibrium constants. These effects of a contacting liquid phase on binding energy, if they were present, would only influence adsorption equilibrium constants in the \( \frac{K_{eq}}{K_i} \) term (eqs 8 and 9) but not H2−D4 exchange rates, which are shown to be insensitive to this term in thermodynamic analysis described above. Changes in rates or kinetic trends resulting from the presence of a liquid would require the (de)stabilization of the TS for kinetically relevant elementary steps with concomitant consequences for their activation free energies (eqs 11 and 12; Scheme 3). Thus, H2−D3 and D2−H2O exchange rates cannot be used to posit any effects of water on the binding of chemisorbed hydrogen. Such information may be obtainable via theoretical calculations (e.g., ab initio molecular dynamics and DFT) that are beyond the scope of our present work but which must be benchmarked for accuracy against our measured rates and their kinetic trends. The experimental data, kinetic trends, and mechanistic assessment presented here, however, stand independently of any theoretical calculations and of any effects of liquid H2O on the binding properties of intermediates. This study shows that H2O−D2 and H2−D3 isotopic exchange kinetics in liquid H2O reflect the prevailing chemical potentials (or fugacities) of gas-phase H2, D2, and H2O in equilibrium with their solvated counterparts. The effects of H2O pressure on H2−D2 and H2O−D2 exchange rates merely reflect the relative coverages of species derived from H2O, D2, and H2 at their respective contacting pressures. While liquid water may indeed affect the work function of metal surfaces, this merely reflects the stabilization of the ejected electron in liquid water (the electron affinity of water, 0.1−0.3 eV)\(^98\)−\(^91\) and not changes in the electronic properties of either bulk metals or, in this case, Pt nanoparticles.

4. CONCLUSIONS

This study rigorously addressed the underlying kinetics of H2O−D2 and H2−D3 isotopic exchange reactions in both gas- and liquid-phase environments. H2O−D2 exchange was shown to occur in the gas phase via the dissociative adsorption of D− and subsequent reaction of chemisorbed D* (at alternative binding modes) with competitively bound H2O*. Such a pathway was shown to be applicable for a wide range of temperatures (up to approximately 900 K) and is reminiscent of our previous work on H2−D2 exchange. The kinetic model for H2O−D2 exchange was further shown to be compatible with our prior H2−D2 exchange model and predictive of H2−D2 and H2O−D2 exchange rates in ternary gas phase H2O−H2−D2 mixtures. The model was then used to probe how changes in the outer-sphere environment affect exchange rates by inducing the formation of a H2O liquid phase within Pt/γ-Al2O3 mesopores. H2−D2 and H2O−D2 exchange rates did not deviate from the gas-phase model even as the catalyst pores were filled, indicating the absence of strong liquid H2O solvation effects. These results reflect the predominant stabilization of TSs by the inner-sphere environment (i.e., Pt surface) for these reactions. The rigorous insights obtained in this study were possible only after extensive purification and degassing of reactant H2O, which otherwise lead to irreversible and confounding titration artifacts. The implications of these results are important for a wide variety of aqueous catalytic processes and provide a framework for rigorously utilizing and interpreting H−D exchange kinetic data in future studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c04678.

Supporting calculations used in methods; N\(_2\) adsorption isotherms on γ-Al2O3; effects of CO\(_2\) contamination on H2−D2 exchange rates; rate equations and kinetic analysis of alternative H2O−D2 exchange mechanisms; derivation of rate equations for H2O−D2 and H2O−H−D2 exchange mediated by reactions of D\(_2\) and H2O*; sensitivity analysis of \( k_0, \frac{K_{eq}}{K_i} \), and \( k_{−s} \) and parity plots for H2O−D2 exchange; and H2−D2 and H2O−D2 isotopic exchange rates in H2O−H2−D2 mixtures (PDF)

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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.

ADDITIONAL NOTE

“As discussed in Section 2.3, turnover rates could not be calculated directly for Pt powders because of uncertain surface areas, but comparisons of temperature sensitivity among samples do not require that rates be normalized by the amount of exposed surfaces.

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