

Heterogeneous Catalysis: Deuterium Exchange Reactions of Hydrogen and Methane

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S Supporting Information

ABSTRACT: Two gas phase deuterium/hydrogen exchange reactions are described utilizing a simple inexpensive glass catalyst tube containing 0.5% Pd on alumina through which gas mixtures can be passed and products collected for analysis. The first of these exchange reactions involves $\text{H}_2 + \text{D}_2$, which proceeds at temperatures as low as 77 K yielding a mixture that includes HD. Products are analyzed by ^1H NMR spectrometry. At low temperatures, this reaction requires a catalyst, but it proceeds without a catalyst at high temperature of a gentle flame. The second deuterium/hydrogen exchange reaction involves $\text{CH}_4 + \text{D}_2$ producing a series of isotopologues, methane- d_x , $x = 0-4$, with product analysis by GC-MS and ^1H NMR spectrometry. This reaction only takes place in the presence of a catalyst at elevated temperatures due to the large energy of activation of the sp^3 -carbon-to-hydrogen bond. Two outcomes have been observed in the literature regarding D/H exchange and methane. Some catalysts and temperature conditions yield a single-exchange result, methane- d_1 . Others yield multiple exchange results, such as we observe with our catalyst. The single exchange outcome is associated with lower temperatures. Two mechanisms, one by Kemball (1959) and one by Frennet (1974), have been put forth to explain single and multiple exchange outcomes. We discuss our results in the context of these mechanisms. Interested readers could develop a research experience for undergraduate chemistry students based on the open-ended experiments presented here.

KEYWORDS: Inorganic Chemistry, Second-Year Undergraduate, Upper-Division Undergraduate, Organic Chemistry, Alkanes/Cycloalkanes, Catalysis, Gases, Isotopes, Transition Elements, Organometallics



In 1836, the Swedish chemist Jöns Jacob Berzelius coined the word *catalyst* in light of some unusual properties of certain substances that had an effect on chemical reactions quite out of proportion with the amount of the substance used. In his words:¹

I shall therefore call it the catalytic power of substances... Catalytic power actually means that the substance is able to awake affinities which are asleep at this temperature by their mere presence and not by their own affinity.

The ensuing 180 years have seen catalysts grow to a \$16.3 billion worldwide industry (2014).² The economic importance of catalysts is summed up in Jens Hagen's book, *Industrial Catalysis: A Practical Approach*.³

The modern industrial world would be inconceivable without catalysts. There is no other technical principle which combines economic and ecological values as closely as catalysis.

Hagen goes on to state that (a) >95% of all products (by volume) are synthesized by catalysis, (b) >80% of all value added in the chemical industry is the result of catalysis, and (c) ~20% of the world economy depends directly or indirectly on catalysts.

This article describes an easily constructed, inexpensive microscale gas-phase catalyst tube that can be used to carry out a wide variety of simple experiments. Over the past decade, we have used catalyst tubes to provide research experiences for undergraduate students.^{4,5} In this paper, we present the basic experimental design for carrying out the reaction between methane and D_2 . We also present the proposed mechanisms described in the literature. The purpose of this paper is to provide background information so that students can design and carry out relatively simple reactions that could shed light on the behavior of the gas mixture with the catalyst. In our experience, almost every experiment suggests others to try, and so the process takes the researchers down a path of inquiry and discovery. Interested readers are directed to Geoffrey Bond's book, *Metal-Catalysed Reactions of Hydrocarbons* for a complete treatment of the literature.⁶

■ BACKGROUND INFORMATION: THE INTERACTION OF HYDROGEN WITH PALLADIUM

Palladium is used as a catalyst in a variety of forms. Reaction chemistry occurring on the surface of crystalline palladium is

the most thoroughly studied as it lends itself to a variety of experimental techniques. Many of the insights into reaction mechanisms are proposed as a result of research involving surface chemistry.^{6–8} When hydrogen is passed over metallic palladium, an interstitial hydride is formed in which hydrogen atoms occupy octahedral holes in the cubic close-packed palladium lattice, followed by atom migration from hole to hole throughout the metal as summarized in Figure 1.^{6,9} Molecular

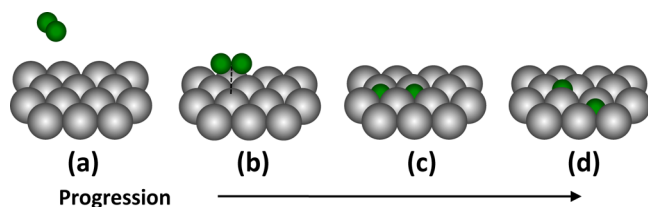


Figure 1. Molecular hydrogen and a Pd(111) surface: (a) Molecular hydrogen (or deuterium) approaches the Pd surface, (b) then binds with the surface (physically adsorbed), (c) cleaves into atoms that occupy octahedral holes within Pd, and (d) readily moves from hole to hole throughout the palladium.

hydrogen is thought to approach the palladium surface and then undergo adsorption with the surface via its H–H σ -bond (agostic bonding) as indicated in Figure 1b. This interaction, albeit ephemeral, brings the H_2 into proximity, whereupon chemisorption takes place. The dissociation of $H_2[Pd]$ into two atoms of hydrogen chemically associated with the palladium, $H[Pd]$, is shown with $b \rightarrow c$ in Figure 1. The hydrogen atoms occupy separate octahedral holes within the palladium, and readily move from hole to hole within the entire Pd framework, Figure 1, $c \rightarrow d$, including being able to burrow down beneath the metal surface. The entire process is reversible and is the basis for hydrogen purification by passing the gas through a foil of palladium as described above.¹⁰ Additional information is provided in the Supporting Information.

■ SMALL METAL PARTICLES

The Pd/alumina catalytic material that we used consists of nanoparticles of palladium situated on 1/8-inch diameter spherical pellets of alumina. Catalytic metals on support materials such as alumina or silica are produced by a wide variety of methods. One approach, relevant to how our Pd/alumina catalyst may have been manufactured, is to imbue the alumina with a solution of $PdCl_2(aq)$. The solution is drawn in by osmosis, in which the alumina acts like a sponge. Water is removed by heating under reduced pressure, and then the Pd^{2+} is reduced with $H_2(g)$ or $CO(g)$.^{6,11} The metal atoms condense into nanoparticles, tiny bits of metal, adhering to the inert and amorphous support material.⁶

Nanoparticles of palladium (and other metals) vary widely in size and shape. In terms of practical applications, nanoparticles of palladium offer an important advantage over macroscopic samples such as foils because of increased surface area. Macroscopic samples feature a relatively small surface area where the catalytic reactions take place. Unlike hydrogen, which burrows deep into the metal and migrates freely throughout the metal, all other molecules can only interact with the surface of the metal. Far larger surface areas are available with small metal particles supported on alumina (or similar materials). These, in turn, provide a more productive use of the palladium as a catalyst. Nanoparticles contain dozens to thousands of atoms

per particle.⁶ From the density of Pd (11.9 g cm^{-3}), one can calculate that a spherical particle of Pd with a radius of 1.0 nm contains about 280 atoms of Pd.¹² (See Supporting Information for full details of all calculations.) The surface area of this spherical particle is $1.3 \times 10^{-13} \text{ cm}^2$. Scaled up to 1.0 g, there are 2.0×10^{19} spherical particles with a combined surface area of $2.5 \times 10^6 \text{ cm}^2$ (250 m^2). This assumes uniform particle size and spherical shapes, both of which do not accurately describe the situation. All nonspherical shapes have more surface area than the sphere; therefore these are fairly rough estimations. Larger spheres have a lower surface area per gram than smaller spheres.

By comparison, the surface area of a 1.0 g piece of Pd foil 0.025 mm thick has a surface area of 67 cm^2 (counting both sides of the foil). Comparing the surface areas of the 1.0 g samples, the 1 nm radius nanoparticles have a surface area that is 37,000 times larger than the same mass of the foil.

The number of atoms on the surface of a Pd sphere with a 1 nm radius can be estimated by calculating the number of core (nonsurface) atoms by assuming the radius of the core is 1 nm minus one diameter of Pd ($2 \times 0.137 \text{ nm}$). This yields ~ 180 core atoms and thus ~ 100 surface atoms per particle. This is significant because all molecules, aside from H_2 and D_2 , can only interact with surface palladium atoms. Larger diameter particles would have a smaller percentage of surface atoms. Calculations such as these described might be an enjoyable challenge to students.

The structure and surface properties of nanoparticles of metals cannot be easily determined, but close-packing is generally assumed. It is estimated that nanoparticles of Pd on an alumina support feature approximately 90% Pd(111) facets as shown in Figure 2.⁸ The rest consists of a variety of crystal

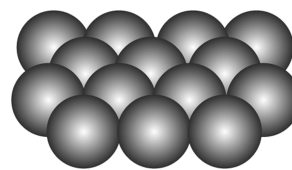


Figure 2. A surface layer of an ideal close-packed lattice.

planes, corners, ridges, partial layers, and so on. While surfaces are rough with partial layers causing the irregular shape of particles, the surface is known to undergo constant remodeling due to the heat generated from chemisorption. Palladium atoms move around on the surface, presumably moving closer and closer to a close-packed structure, palladium's standard state structure. In fact, Bond describes the situation as (ref 6, p 68), "A small metal particle may comprise a solid core and a semi-fluid surface layer."

While a catalyst of Pd particles supported on alumina beads is not the same as metallic elemental palladium as described above, the differences do not usually change the fundamental steps of the reaction mechanism.^{6,13} In both cases, local surfaces can be represented by the metal atoms shown in Figure 2.

■ EXPERIMENTAL SECTION

Palladium/Alumina Catalyst Tubes

At the center of the experimental apparatus is a 6 mm diameter (OD) glass U-tube containing alumina beads coated with 0.50% palladium (Figure 3). In this article we use catalyst tubes

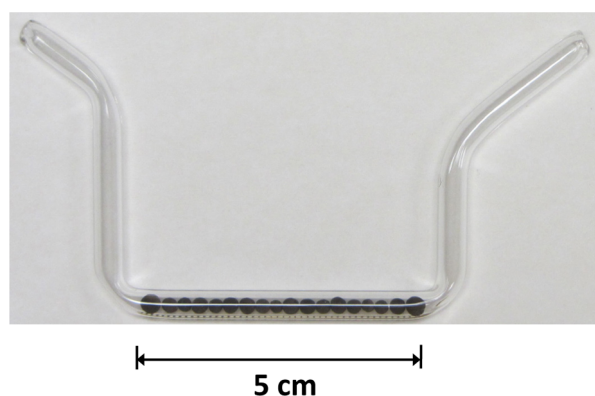


Figure 3. Homemade catalyst tube containing 0.5% Pd on alumina. The U-shape allows the catalyst to be temperature-controlled in a bath.

built by students to study D/H exchange between (a) $\text{D}_2(\text{g}) + \text{H}_2(\text{g})$ and (b) $\text{D}_2(\text{g}) + \text{CH}_4(\text{g})$. The catalyst tube shown in Figure 3 contains 0.252 g of Pd/alumina beads. This corresponds to 1.3 mg of Pd or 1.2×10^{-5} mol of Pd atoms. If we assume the median radius of the nanoparticle is 1 nm,¹⁴ there is 4.2×10^{-6} mol of Pd atoms situated on the surfaces. This particular catalyst tube would then contain 2.5×10^{16} nanoparticles of average radius 1 nm, with a total surface area of 0.32 m^2 : the same as 47 g of 0.025 mm thick Pd foil. Catalyst tubes such as the one pictured in Figure 3 cost less than \$2 in materials.

The 6 mm OD glass tubing used to make our catalyst tubes has a measured volume of 0.10 mL/cm. This value was determined by filling the tube with water, measuring its mass and length, and then using density to convert mass to volume and then volume/length. Thus, the 5 cm length of tubing containing the catalytic beads has a volume of 0.50 mL, much of which is occupied by the beads. The volume of the beads is estimated from the average diameter of the beads, 1/8-inch, given on the product specifications. Together these beads occupy a total volume of $\sim 0.3 \text{ mL}$, leaving $\sim 0.2 \text{ mL}$ for the gas. In typical experiments such as the one described here, the syringe contains a mole fraction of reactants that is 1/3 CH_4 and 2/3 D_2 . At 350°C and $\sim 1 \text{ atm}$, this corresponds to $\sim 4 \times 10^{-6}$ mol of total gas, or $\sim 1.3 \times 10^{-6}$ mol of CH_4 in a 1:2 mixture of $\text{CH}_4:\text{D}_2$. The ratio of surface Pd atoms to CH_4 molecules is $\sim 4.2 \times 10^{-6}$ mol of surface Pd atoms to 1.3×10^{-6} mol of CH_4 or $\sim 3 \text{ Pd}$ to 1 CH_4 .

Much of the mechanistic work described in the literature utilizes sophisticated equipment, precise experimental technique, and considerable amounts of time and money. We are not attempting to duplicate this work, but rather to establish how simple and inexpensive experiments can lead to conclusions and suggest further experiments. Any number of variations of the experiments described here could be designed, all with our catalyst tube. Experiments are also inexpensive, and can be performed by undergraduate research students in short periods of time. (A mass spectrometer and ^1H NMR spectrometer are necessary for analysis, however.)

Detailed instructions for the construction of the catalyst tube and for all experimental procedures are given in the Supporting Information. The assembled apparatus consists of the U-shaped catalyst tube connected to two 60 mL syringes with short pieces of latex tubing. One syringe holds the reagents: for the $\text{H}_2(\text{g}) + \text{D}_2(\text{g})$ D/H exchange experiment, 30 mL of each gas is used. For the methane + deuterium D/H exchange experiment, 20

mL of $\text{CH}_4(\text{g}) + 40 \text{ mL}$ of $\text{D}_2(\text{g})$ is used; the latter provides an equal mole amount of D and H atoms. The second syringe for both experiments is the empty receiver syringe.

Time spent in the presence of the catalyst is called the residence time. With a typical flow rate of 1 mL per 4 s, and a gas volume in the presence of the catalyst of 0.2 mL over the length of 5 cm, the residence time is 0.8 s. In order to ensure that the reagents have an average residence time with the catalyst, the flow rate must be as constant and steady as possible. A homemade syringe pump, suitable for handling a 60 mL syringe and delivering a steady flow of gas, is described in the Supporting Information.

Temperatures are measured with a bimetallic thermocouple.

HAZARDS

Manipulating gases in syringes is generally safe, and unintentional discharges are not common. Nevertheless, such discharges are possible, and it is important to remember that all of the gases used are highly flammable and form explosive mixtures with air. If catalyst tubes are being constructed, palladium catalyst beads should be handled with gloves (e.g., disposable latex or nitrile). Prudent safety measures must be employed when open flames are used to bend glass to prepare the catalyst tubes and when conducting the reaction using a burner as a heat source. Burners should never be used in the vicinity of flammable materials or left unattended. Loose clothing and long hair should be secured to prevent contact with the flame. Others present in the lab should be made aware that a burner is in use. A fire extinguisher should be readily available.

RESULTS AND DISCUSSION

$\text{H}_2(\text{g})$ and $\text{D}_2(\text{g})$ D/H Exchange

When equimolar mixtures of $\text{H}_2(\text{g})$ and $\text{D}_2(\text{g})$ are passed over palladium/alumina (flow rate $\sim 2 \text{ mL/s}$), D/H exchange occurs even at very low temperatures according to the reaction $\text{H}_2(\text{g}) + \text{D}_2(\text{g}) \rightleftharpoons 2 \text{ HD}(\text{g})$ as depicted in Figure 4.

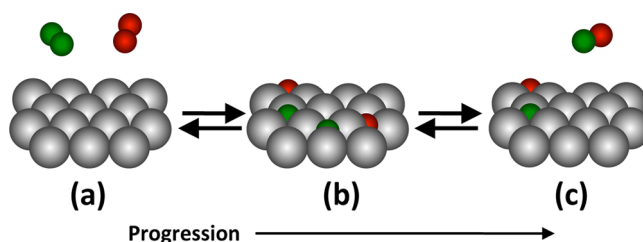


Figure 4. (a) A mixture of H_2 and D_2 is passed over the Pd catalyst; (b) chemisorption leads to atoms of H or D moving freely throughout the network of holes; and (c) D and H atoms are released as HD. Both processes $a \rightarrow b$ and $b \rightarrow c$ are reversible.

At 77 K, only a small amount of HD is detected by ^1H NMR spectroscopy. Larger amounts of HD are detected at higher temperatures and/or with slower flow rates. At the temperature of a gentle flame ($\sim 525^\circ\text{C}$), D/H exchange occurs even without the catalyst present. At temperatures below 350°C , the reaction can only take place in the presence of the catalyst.

The ^1H NMR spectrum shown in Figure 5 is the result of an experiment in which a mixture consisting of 30 mL of $\text{H}_2(\text{g})$ and 30 mL of $\text{D}_2(\text{g})$ was passed through the catalyst tube over the course of 30 s at 0°C . Molecular $\text{H}_2(\text{CDCl}_3)$ has a

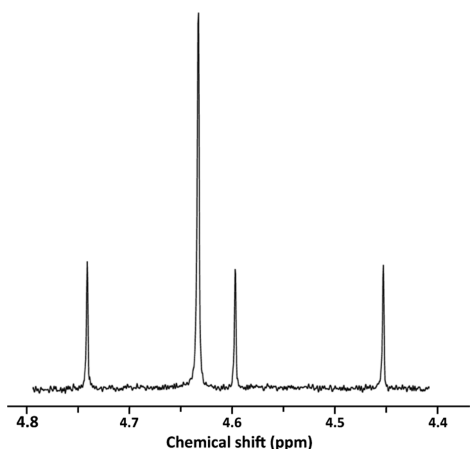
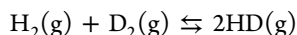


Figure 5. ^1H NMR spectrum of H_2 and DH at ambient temperature in CDCl_3 .

chemical shift of $\delta = 4.634$ ppm. Molecular $\text{HD}(\text{CDCl}_3)$ appears as a triplet, $\delta = 4.599$ ppm, $J_{\text{HD}} = 42.7$ Hz. (The nuclear spin, I , equals 1 for deuterium, so a triplet is observed resulting from $I = -1, 0$, and $+1$ in near-equal proportions.) The chemical shift for HD is shifted upfield from that of H_2 as expected due to the extra shielding caused by the deuterium atom.

Integration of the ^1H NMR peaks yields a reaction quotient, $Q_c = [\text{HD}]^2/[\text{H}_2][\text{D}_2] = 1.6$.¹⁵ The literature value¹⁶ for the equilibrium constant, $K_c = [\text{HD}]^2/[\text{H}_2][\text{D}_2]$, is



$$K_c^{273\text{K}} = 3.24; K_c^{298\text{K}} = 3.28; K_c^{\text{large-temperatures}} \sim 4$$

In this particular experiment the reaction did not yield an equilibrium mixture during the brief time the gases were in the presence of the catalyst; D/H exchange was incomplete. Gases not in the presence of the catalyst are frozen in formula as H_2 , D_2 , or HD .

Methane and Deuterium Exchange

In our experiments, D/H exchange between $\text{CH}_4(\text{g})$ and $\text{D}_2(\text{g})$ only occurs at high temperatures. Methane, like alkanes in general, requires elevated temperatures for carbon–hydrogen bond activation to occur. In a study involving ethane and a platinum(111) single crystal, the C–H bond activation energy was measured to be 79 kJ/mol.¹⁷ We used a heated sand bath to achieve temperatures in the range 300–450 °C, and a gentle

flame for higher temperatures, ~500–550 °C. When performing experiments in a flame, a straight version of the catalyst tube is used. At temperatures below ~300 °C, extensive D/H exchange does not occur. For comparison purposes, ethene + D_2 and 1-butene + D_2 undergo D/H exchange at 0 °C with our catalyst tube, as described in our previous paper.⁵

A single, successful D/H exchange will produce CH_3D , (methane- d_1). The enthalpy change for this reaction is very small due to the similarity of the reactant and product.¹⁸ Multiple exchanges are also possible, and all together five isotopologues are possible, CH_4 (methane- d_0), CH_3D (methane- d_1), CH_2D_2 (methane- d_2), CHD_3 (methane- d_3), and CD_4 (methane- d_4).

Bond dedicates an entire chapter to deuterium exchange with alkanes.⁶ D/H exchange with alkanes is ostensibly the simplest of all catalytic changes that could occur to an alkane. Most careful studies take place at reduced pressures utilizing the methods of surface science. In the majority of studies referenced in Bond's book, a 10-fold excess of D_2 was used, an experimental design that minimized the reverse reaction and allowed researchers to identify initial products, thereby providing glimpses into the mechanisms.

Two Mechanisms for D/H Exchange in Methane

Two different mechanisms for D/H exchange are important for alkanes, including methane. The first is the *single exchange* (also called *stepwise exchange*) in which only one atom is substituted during each encounter with the Pd surface. The other mechanism is the *multiple exchange* in which D/H exchange is more extensive. In surface studies employing excesses of deuterium, the single exchange mechanism produces predominantly methane- d_1 , and the multiple exchange mechanism produces predominantly methane- d_4 .^{6,19} In fact, in some studies, the two mechanisms occur simultaneously, initially yielding methane- d_1 and methane- d_4 , but little or no methane- d_2 and methane- d_3 .^{6,19} The single exchange mechanism predominates for methane at lower temperatures.^{6,20–22}

In 1959, Kemball proposed a reaction pathway for both the single exchange and multiple exchange reaction pathways.²¹ Kemball's single exchange mechanism involves $\text{CH}_3[\text{Pd}]$ as an intermediate, and the multiple exchange mechanism involves $\mu\text{-CH}_2[\text{PdPd}]$ as an intermediate. Fifteen years later, in 1974, Frennet proposed an alternative sequence to account for the two reaction pathways.²¹ Frennet's single exchange mechanism involves a concerted interaction between CH_4 and $\text{D}[\text{Pd}]$ with no Pd–C bond formation, and the multiple exchange

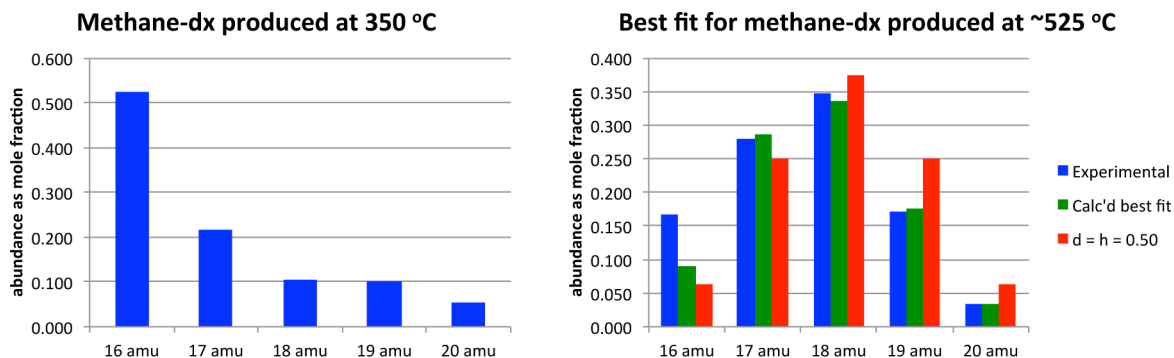


Figure 6. Mass spectrum of methane- d_x produced by passing $\text{CH}_4 + \text{D}_2$ through the Pd/alumina catalyst tube (a) at 350 °C and (b) in a gentle flame (~525 °C). The blue columns represent abundances, displayed as mole fractions. Green columns represent best fit for masses 17–20; in this example, $d = 0.46$ and $h = 0.54$. The red columns represent the pattern that results if $d = h = 0.50$, where d and h are the mole fractions of D and H.

mechanism that seems much the same as Kemball's single exchange mechanism. Their proposed mechanisms are presented in more detail in the [Supporting Information](#).

Both of the mechanisms of Kemball and Frennet explain the basic facts of D/H exchange between CH₄ and D₂. Bond lists a number of questions left unanswered by both mechanisms, all quite technical and beyond the scope of this article. Bond also notes (ref 6, p 266), "there has been no study of methane exchange on any single crystal surface because of insuperable practical difficulties".

Mechanisms involving radical species may be possible at even higher temperatures, however, we have run control experiments in which we passed D₂ + CH₄ through an empty (no Pd) tube and observed no D/H exchange even at 525 °C. This is particularly remarkable because H₂ + D₂ undergoes D/H exchange at this temperature even without the Pd catalyst present. Thus, we can rule out exchange pathways such as CH₄ + D• → CH₃D + H•.

Our Results CH₄ + D₂ D/H Exchange

Our experiments with our catalyst tubes seem to suggest that methane either (a) passes over the catalyst unchanged or (b) undergoes a series of D/H exchanges.

In a typical experiment, we pass mixtures of 20 mL of CH₄(g) + 40 mL of D₂(g) through our catalyst tube at a controlled temperature and flow rate, and then analyze the mixture by gas chromatography–mass spectrometry and ¹H NMR spectrometry. The results of two experiments at different temperatures are given in [Figure 6](#). The figure on the left is the mass spectrum from an experiment conducted at 350 °C with a flow rate of 0.25 mL/s. All five isotopologues are observed. The peak at mass 16 is mostly due to unreacted CH₄, representing ~45% of the methane, that passed through the catalyst. Masses 17, 18, 19, and 20 correspond to CH₃D, CH₂D₂, CHD₃, and CD₄, respectively.²³

When the reaction is conducted with the catalyst tube held in a gentle flame (~525 °C) at a flow rate of 0.25 mL/s, the product mixture affords the mass spectrum given in [Figure 6b](#).²⁴ The columns in blue represent the observed mass spectrum, with abundances presented as mole fractions.

The columns in green in [Figure 6b](#) represent the calculated mass spectrum that provides the best fit with the observed results. The columns in red represent the calculated mass spectrum if equal moles of deuterium and hydrogen atoms were used to form the five isotopologues. The formulas used to produce these patterns are $f_{16} = h^4 \times d^0 \times 1$, $f_{17} = h^3 \times d^1 \times 4$, $f_{18} = h^2 \times d^2 \times 6$, $f_{19} = h^1 \times d^3 \times 4$, and $f_{20} = h^0 \times d^4 \times 1$, where f_{16} is the mole fraction of isotopologues with mass 16, and so on. The variables h and d are the mole fractions of H and D, respectively. The numbers 1, 4, 6, 4, and 1 represent the number of different permutations that would yield each particular mass. For example, there are 4 ways to place a deuterium atom on CH₃D.

When $h = d = 0.5$, a symmetrical pattern results as shown with the red columns.²⁵ This particular pattern is singled out because 20 mL of CH₄ + 40 mL of D₂ provides equal number of moles of D and H in the reaction mixture.

The green columns represent the best fit for masses 17–20, ignoring mass 16 as it contains unreacted methane. The above formulas were used to calculate every possible mass spectrum ranging from $d = 0.00$ to $d = 1.00$, in increments of 0.01. Comparing the experimental mass spectral results with the theoretical mass spectral results for masses 17–20 yields a best

fit for $d = 0.46$ and $h = 0.54$. The difference between the experimental (blue) abundance for mass 16 and the calculated abundance (green) is the unreacted methane, and it represents ~8% of the methane used. Full details for the mass spectral modeling are given in the [Supporting Information](#).

The ¹H NMR spectrum of the isotopologic mixture produced at ~525 °C is presented in the [Supporting Information](#). Methane-*d*₀ appears at $\delta = 0.248$ ppm. With each additional deuterium atom added, the chemical shift moves upfield by $\delta = 0.233$ ppm as expected due to the additional shielding provided by deuterium. Resonances for CH₃D, CH₂D₂ ($\delta = 0.218$ ppm), and CHD₃ ($\delta = 0.204$ ppm) are all observed and readily identified by the D/H coupling patterns.

DISCUSSION

Kemball's and Frennet's mechanisms, described in the [Supporting Information](#), were proposed to explain the two scenarios encountered when studying the interaction of methane with D[Pd] under conditions of low pressure of CH₄ with a large excess of deuterium on a metal surface. The single exchange mechanism results in mostly CH₃D and is associated with lower temperatures than the multiple exchange mechanism, which can result in mostly CD₄. Our reactions, in contrast, were conducted at ~1 atm pressure with reaction mixtures where the moles of hydrogen atoms from CH₄ and deuterium atoms from D₂ were equal. At the temperature used for our experiments (300–525 °C), we observe all five isotopologues of deuteromethane. Our reaction conditions are so different from those employed by surface chemists, can we use the ideas of Kemball and Frennet to understand our experimental results?

Starting with the single exchange mechanism, the result of multiple occurrences of the single exchange reaction would be equivalent to the multiple exchange outcome. In our flow experiments, methane molecules move past the catalyst, eventually leaving the catalyst tube, and are frozen in formula: no additional D/H exchange can take place. For example, if the single exchange occurred twice for a particular methane molecule traveling through the catalyst tube, we would see CH₄, CH₃D, and CH₂D₂ because the catalyst contains both H[Pd] and D[Pd]. The strongest evidence against the repeated single exchange explanation comes from the significant amount of unreacted CH₄: Why would some molecules undergo repeated single exchanges while others did not undergo any? The counterarguments include the following: (a) At temperatures that are suitable for the higher temperature mechanism (multiple exchange) to take place, the lower temperature mechanism (single exchange) takes place even faster, so we are certain it is happening; and (b) If the mole ratio of surface Pd atoms to methane molecules is low as estimated above, there may be relatively few open Pd sites with which methane may interact, so some molecules pass through the catalyst tube without finding a site. A newly released free methane-*d*₁ molecule would also have the advantage of proximity to the newly vacated Pd site, which could lead to another single exchange.

The multiple exchange mechanisms are in competition with the reductive elimination of free methane-*d*_x. Frennet's multiple exchange mechanism starts with oxidative addition (chemisorption) of methane, CH₄ + Pd → CH₃[Pd] + H[Pd], followed by the sequential one-site deuteration of Pd-bound methyl groups: CH₃-[Pd] → CH₂D-[Pd] → CHD₂-[Pd] →

$\text{CD}_3\text{-[Pd]}$, and then reductive elimination of CD_4 . Since the mechanism requires reductive elimination of free CD_4 as the last step, it follows that each of the moieties $\text{CH}_x\text{D}_{3-x}\text{-[Pd]}$ could also undergo reductive elimination of free methane- d_x , $x = 0\text{--}4$. It also follows that each of the nascent deuteromethanes could undergo a subsequent oxidative addition such as the mechanism calls for in the first step, and the process starts anew.²⁶ Under conditions with large excess of deuterium in surface studies, CD_4 is predominantly observed.¹⁹ Why are less-deuterated products not observed, such as CHD_3 , etc.? One can conclude either (a) D/H exchange is significantly faster than reductive elimination so that exchange of H for D is complete due to the vast excess of D before reductive elimination occurs, or (b) the multiple exchange process happens several times before the free methane- d_4 leaves the area with the catalyst. It is also reasonable to expect that the single exchange mechanism is occurring at temperatures required for the multiple exchange mechanism.

In our experiments, nearly equal moles of D and H atoms were present, so if D/H exchange went to completion, the mass spectral pattern shown in red in Figure 6b would result. Methane enters the reaction zone with four H atoms. Where the gas mixture ($\text{CH}_4 + \text{D}_2$) first encounters the Pd, the Pd is expected to be rich in D[Pd] , although the D atoms quickly migrate throughout the Pd. With each exchange of $\text{H} \rightarrow \text{D}$, the Pd catalyst gains an H[Pd] , and eventually the number of moles of H[Pd] approaches the number of moles of D[Pd] . Only in the limit of complete D/H exchange would one expect a pattern of isotopologues that features as much D as H. In the context of our experiments, complete D/H exchange is a localized equilibrium situation occurring between methane- d_x molecules and H/D[Pd] in which the rate of exchange $\text{H} \rightarrow \text{D}$ equals the rate for $\text{D} \rightarrow \text{H}$. In a flow system such as we use, this may occur for those molecules that have been in the presence of the catalyst for a suitable length of time. Reductive elimination of methane- d_x is a competing reaction and may lead to less deuteration in the methane reaction products than the 1:1 ratio of D and H would predict because some of the newly freed methane molecules will be swept past the catalyst by the flow conditions before they can undergo an additional exchange process. This would explain why the best fit for our reaction products corresponds to 54 mol % H and 46 mol % D at $\sim 525^\circ\text{C}$. In fact, the amount of deuterium, D[Pd] , available for reaction exceeds hydrogen, H[Pd] , because of the methane that passes through the catalyst as unreacted CH_4 , thereby withholding H atoms from the Pd. In summary, the number of moles of D[Pd] exceeds the number of moles of H[Pd] , but the best fit for the methane- d_x observed in the product has fewer moles of D than H.

It is worth noting that we have never seen any evidence of carbon–carbon bond formation in our mass spectral results, which would appear as masses 30–36 for ethane- d_x .

SUMMARY

The deuterium/hydrogen exchange experiments performed with our Pd/alumina gas catalyst tube give extensive exchange in both of the experiments described here: (a) equimolar mixtures of $\text{D}_2 + \text{H}_2$ at 0°C , and (b) methane + D_2 at ~ 350 and 525°C . In our previous work with ethene and 1-butene,⁵ we also reported extensive D/H exchange, but under very mild conditions (ice bath). The chemisorption of H_2 and D_2 with Pd occurs at extremely low temperatures, despite the enormous H–H covalent bond energy, and is in fact exothermic. The path

is paved by the affinity between σ -bond of H_2 and Pd, which holds the molecule in place while chemisorption takes place. Alkenes initially bond to Pd through their π -manifold, and D/H exchange occurs as a result of the Horiuti–Polanyi mechanism for hydrogenation.²⁷ Alkanes, with their sp^3 -hybridized carbon, have no such methods of initially interacting with the palladium, and undergo carbon–hydrogen bond activation (possibly through agostic C–H bond interaction with Pd) only at temperatures $>300^\circ\text{C}$ resulting in multiple D/H exchanges in the short amount of time methane in the presence of the catalyst. Under our reaction conditions, the observed D/H exchange could occur by the multiple exchange pathway or several single exchange events, or a combination thereof. Open questions suitable for inquiry-based undergraduate research projects based on our results are provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00360.

Instructions, ordering information, description of spreadsheet used to model methane mass spectral patterns, and all of the spectra obtained (PDF)

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Notes

The authors declare no competing financial interest.

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(12) One could also calculate the volume of a 1.0 nm radius sphere and the volume of one Pd atom, adjust the sphere for the 74% packing efficiency exhibited by fcc lattices, and calculate the number of atoms by dividing the adjusted sphere volume by the volume of an individual Pd atom.

(13) There are differences in reactivities between solid Pd and small particles of metal. For example, from a temperature-programmed desorption (TPD) study, ethene does not undergo hydrogenation using metallic (single crystal) palladium, whereas it does using Pd particles on alumina (the catalyst we use in this article).^{7,8} The explanation is that, under TPD conditions, hydrogen atoms migrate deep within the Pd in macroscopic samples of Pd and are no longer accessible for hydrogenation; however, in Pd nanoparticles, hydrogen atoms cannot get too far away from the surface and hydrogenation occurs.

(14) This is only an assumption for the sake of discussion. Based on Bond's range of particle sizes, $\sim 10^1$ – 10^4 ,⁶ we used a 1 nm radius which gives a particle with ~ 280 atoms, within Bond's range.

(15) Q_c was determined as follows: The sum of the integrations of the three peaks of the triplet represents one equivalent of HD, while the large singlet represents two equivalents of hydrogen, H₂. D₂ does not appear, but should be mole equivalent to H₂.

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(18) Bond points out (Chapter 6) that the D/H exchange between CD₄ + H₂ is slower than CH₄ + D₂. Furthermore, E_{act} between n -C₆D₁₄ + H₂ on Pd film is 4 kJ/mol greater than n -hexane + D₂.

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(23) ¹³C accounts for 1.109% of all carbon, and naturally occurring ²H accounts for 0.0156% of all hydrogen. Collectively, 1.17% of methane has a mass of 17 due to one or the other of these isotopes. This is a negligible amount in the context of our calculations.

(24) At even low ionization energies, some fragmentation (loss of H or D) occurs giving rise to a peak at mass 15, some from CH₄ losing H and some from CH₃D losing D. We adjusted the mass spectrum by redistributing mass 15 back to masses 16 and 17. Details are provided in the [Supporting Information](#).

(25) Deuterium isotope effects are not taken into account, but are expected to be small, especially at high temperatures.

(26) An analogous discussion could be developed for the Kemball multiple exchange mechanism.

(27) These results are summarized in the [Supporting Information](#) and presented in detail in our previous article in this journal.⁵