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COMMUNICATION

Theoretical analysis of the reaction mechanism of D_2 gas generation using a Pd/C catalyst

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Efficient D_2 gas generation is crucial for synthesizing deuterated compounds. This study reveals that D_2 forms via the Grotthuss mechanism in a D_2O–H_2 system on a Pd/C catalyst. The process involves a D_2O–H* interaction forming an HD_2O* intermediate and proton-electron transfer, transferring charge to the metal surface.

In recent years, deuterium, an isotope of hydrogen, has gained recognition for its applications in organic chemistry and various other fields, including drug development[1,2] and digital communication.[3] For example, highly efficient medicines have been developed via deuteration-based enhancement of the durability of involved compounds[1,2] through substitution of C–H bonds by C–D bonds, which are more stable owing to their larger bond dissociation energy. In addition, deuteration[3] can reduce optical loss in optical fibers by shifting vibrational absorption to high wavelengths. Several efficient H/D exchange reactions and D_2 gas generation using catalysts have been explored to produce deuterated compounds.[4-8] We[5] demonstrated an efficient H_2/D_2 exchange reaction in a D_2O–H_2 system using a heterogeneous catalyst, 10% Pd/C (Scheme 1), leading to D_2 gas generation. Although the H_2/D_2 exchange reaction between the D_2O solvent and H_2 gas is speculated to occur on the metal surface, the detailed reaction mechanism remains unclear.

$$2D_2O + H_2 \xrightarrow[\text{rt}]{\text{10\% Pd/C}} 2DHO + D_2$$

Scheme 1 D_2 gas generation via H/D exchange.

Several H/D exchange mechanisms for the exchange reaction between D_2O and H_2 on metal surfaces have been proposed based on experimental results.[9-11] Mironenko et al.[9] suggested that H_2 and D_2O dissociatively adsorb onto metal surfaces, followed by HDO desorption. However, several studies have suggested that the reaction proceeds via the Grotthuss mechanism, where D_2O does not undergo dissociative adsorption. Instead, an HD_2O* intermediate is formed with D_2O and adsorbed H* on the metal surface of the Pd/C catalyst, leading to an H/D exchange reaction.[10,11] Pan et al.[10] analyzed the interaction between H atoms adsorbed on the Au and H_2O molecule surfaces and postulated that the H/D exchange reactions between the adsorbed H(D) atom and $H_2O(D_2O)$ molecules occurred via the formation of a H-bonding network (i.e., formation of $H^+(H_2O)_n$). Further, Bonnin et al.[11] investigated the reaction mechanism of glucose hydrogenation on supported metal catalysts using the H/D exchange reaction. They observed the formation of HOD, HD, and D_2 molecules in a H_2–D_2O system and speculated that D_2 gas generation is a stepwise reaction, in which HD gas is formed in the first step and acts as a reactant in the second step to produce D_2 gas (Scheme 2).

$$D_2O + H_2 \xrightarrow[\text{rt}]{\text{10\% Pd/C}} DHO + HD$$

$$D_2O + HD \xrightarrow[\text{rt}]{\text{10\% Pd/C}} DHO + D_2$$

Scheme 2 D_2 gas production reaction from H_2.

Theoretical analyses are valuable for elucidating reaction mechanisms. However, the detailed mechanism of the H_2/D_2 exchange reaction has not been theoretically analyzed because most conventional quantum chemical calculation methods do not account for nuclear quantum effects (NQEs) due to the Born–Oppenheimer approximation (BOA). These methods can

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only capture differences in the zero-point vibrational energy between H and D but not the geometrical differences between nondeuterated and deuterated compounds. In contrast, we previously developed a multicomponent density functional theory (MC_DFT), which can incorporate the NQEs of protons and deuterons beyond BOA.[12-14] The MC_DFT can represent H/D isotope effects on the energies and the electronic structures and geometrical parameters. Therefore, we aim to reveal the H/D exchange reaction mechanism in the D_2O–H_2 system using the MC_DFT.

Herein, we assumed that the H/D exchange reaction (Scheme 1) occurred on the Pd surface of the carbon-supported metal catalyst (Pd/C), and a two-layer Pd_{22} cluster was used to model the Pd(111) surface. Kunimoto[15] revealed the mechanisms of HPO_2^{2-} adsorption on Pd surfaces using the two-layer Pd_{22} cluster model. Consequently, we believe that this cluster model is adequate for the present purpose. The APFD exchange–correlation functional[16] and 6-31G** basis set for H and O atoms were adopted. For Pd atoms, the LANL2DZ effective core potential and basis set were adopted. In MC_DFT calculations, all H and D nuclei were quantum mechanically treated. A single s-type Gaussian-type function, $\exp\{-\alpha(r-R)^2\}$, was used for the protonic and deuteronic basis functions. The α values in the nuclear basis functions for protons and deuterons were set to 24.1825 and 35.6214, respectively[13]. All calculations were performed using the modified version of the Gaussian16 program package.

We assumed that the H atoms in the H_2 molecule were deuterated one by one in the H_2/D_2 exchange reaction and investigated the two reaction mechanisms presented in Scheme 3. In mechanism (a) (Scheme 3(a)), both H_2 and D_2O molecules undergo dissociative adsorption on the metal surface and participate in the H/D exchange reaction.[9] Meanwhile, in mechanism (b) (Scheme 3(b)), only the H_2 molecule undergoes dissociative adsorption on the Pd surface and forms an HD_2O^* intermediate by reacting with D_2O.[11]

To analyze mechanism (a), we initially calculated the energy diagrams for the dissociative adsorption reactions of the H_2 and D_2O molecules (Fig. 1).

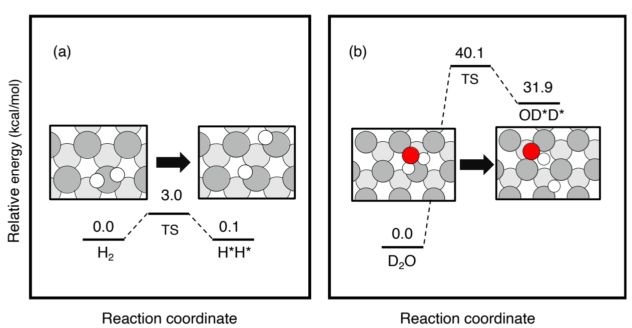
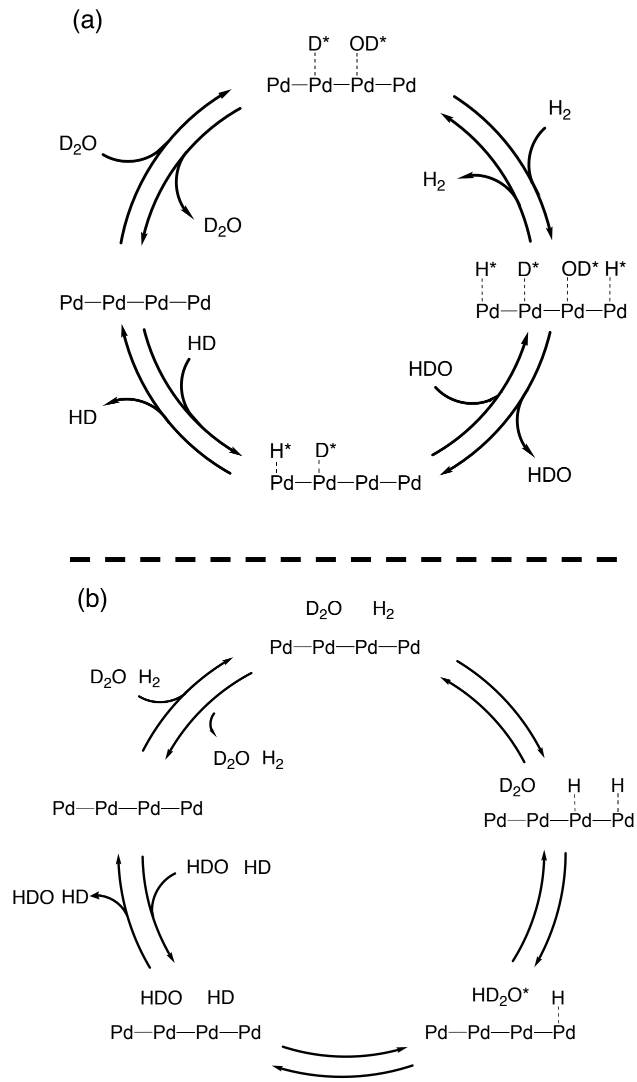


Fig. 1 Energy diagrams of the dissociative adsorption reactions of (a) H_2 and (b) D_2O on the Pd_{22} cluster model obtained through MC_DFT calculations.

By focusing on the dissociative adsorption of H_2 (Fig. 1(a)), the activation energy was obtained as 3.0 kcal/mol, indicating that the adsorption easily occurs; the reverse reaction was also



Scheme 3 H/D exchange mechanisms proposed in this study. (a) Both H_2 and D_2O are adsorbed on the metal surface before the formation of HDO and (b) H/D exchange reaction occurs via HD_2O^* formation by H* with D_2O.

likely to occur. This result is consistent with previous experimental and theoretical results.[15,16] Meanwhile, the activation energy for the dissociative adsorption of D_2O (Fig. 1(b)) was 40.1 kcal/mol and the relative energy of the product (OD*D*) was 31.9 kcal/mol, suggesting that this reaction was unlikely to occur. From these considerations, we speculate that the reaction in Scheme 3(a) would likely not occur owing to the large activation energy required for the D_2O dissociation step. Various studies have investigated the dissociative adsorption reaction of H_2O on the Pd(111) surface and concluded that dissociative adsorption did not occur on a clean surface.[17,18] Thus, the abovementioned MC_DFT results are consistent with the results of previous studies.

Next, mechanism (b) (Scheme 3(b)) was investigated. This reaction is considered to proceed in three steps. Step 1: The H_2

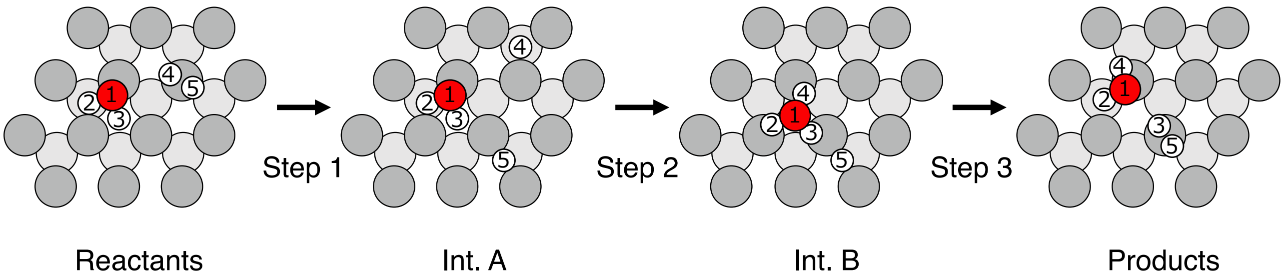


Fig. 2 Reaction mechanism via an HD_2O^* intermediate for the D_2O–H_2 and D_2O–HD systems.

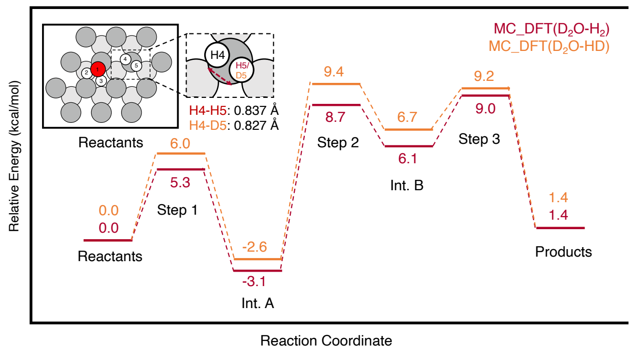


Fig. 3 Energy diagram for the H/D exchange reaction between D_2O and H_2/HD on the Pd surface calculated using the MC_DFT. The red and orange lines represent results of the D_2O–H_2 and D_2O–HD systems, respectively.

molecule dissociates and adsorbs on the metal surface to form an intermediate (Int. A), in which H atoms are bonded to the metal atoms. Step 2: An HD_2O^* intermediate (Int. B) is formed by an H* atom and a D_2O molecule on the metal surface. Step 3: A D atom is extracted from Int. B by the other H* atom to form HDO and HD molecules.

Fig. 3 presents the energy diagram for mechanism (b) obtained through MC_DFT calculations. In addition to the D_2O–H_2 system, we investigated the D_2O–HD system, which produced HDO and D_2 molecules. First, we focus on the D_2O–H_2 system (represented by the red lines in Fig. 3). Step 1 was exothermic, with an activation barrier of 5.3 kcal/mol, which is not very high. This suggests that the dissociative adsorption of H_2 is likely to occur consistently with the aforementioned results (Fig. 1). Meanwhile, the activation energy for Step 2 was 11.8 kcal/mol, which is the largest in this reaction pathway. Therefore, Step 2 is the rate-limiting step of the reaction mechanism. In Step 3, a D atom was desorbed from HD_2O^*. The activation barrier for Step 3 was only 2.9 kcal/mol, indicating that Step 3 easily proceeds. Because this reaction mechanism did not have any insurmountably large activation barriers, the proposed H/D exchange reaction mechanism seems to be the most plausible.

We now focus on the D_2O–HD system (indicated by the orange lines in Fig. 3). The energy diagram for the D_2O–HD system slightly differs from that for the D_2O–H_2 system. The activation energy for Step 1 and the relative energy for Int. A in the D_2O–HD system was 6.0 and −2.6 kcal/mol, respectively, which are slightly higher than those in the D_2O–H_2 system. The H4–D5 bond length was 0.827 Å, which is smaller than the H4–H5 bond length (0.837 Å); the MC_DFT reproduced the H/D geometrical isotope effect, which led to a higher activation barrier. Consequently, HD dissociation was less likely to occur than H_2 dissociation. We believe that the H/D isotope effects influenced the generation timing of the HD and D_2 gases, as explained by Bonnin et al.[11] Further, because the activation energy for Step 2 was only slightly higher than that for Step 2 in the D_2O–H_2 system, we predicted that the D_2 gas generated similarly to the HD gas generation. In other words, the H_2/D_2 exchange reaction proceeded in a stepwise manner as shown in Scheme 2.

To analyze the charge transfer between the adsorbed molecules and metal surface, we focused on the electronic structure of Int. B. We analyzed the changes in the atomic charges during the H/D exchange reactions to gain insights into the charge transfer between the adsorbed molecules (atoms) and metal surface. Fig. 4 shows the total natural atomic charges for each structural group (the charge of each atom is shown in SI) obtained by natural bond orbital (NBO) analysis.

As shown in Fig. 4, the charge of the Pd cluster substantially changed in Step 2 (from −0.459 to −0.950 in the D_2O–H_2 system and from −0.451 to −0.939 in the D_2O–HD system). O1, D2, D3, and H_4 formed the HD_2O^* structure in Int. B and the sum of their atomic charges were +0.826 and +0.825 in the D_2O–H_2 and D_2O–HD systems, respectively, suggesting that HD_2O^* existed as HD_2O^+ and H4 was transferred as a proton. Several scholars have observed hydrated protons on metal surfaces, such as oxonium ion (H_3O^+), Zundel cations ($H_5O_2^+$), and Eigen cations ($H_9O_4^+$).[10,21] This indicates that charge transfer occurred between the metal surface and adsorbed molecules in Step 2.

Finally, we examined the stability of the generated D_2 molecule by analyzing the D/H exchange reaction between HDO and D_2 molecules (Scheme 4). The same mechanism as the H/D exchange reaction (Fig. 2) was assumed for the D/H exchange reaction. Fig. 5 shows the energy diagram for the D/H exchange reaction calculated using the MC_DFT.

$$HDO + D_2 \longrightarrow D_2O + HD$$

Scheme 4 D/H exchange reaction in the HDO–D_2 system.

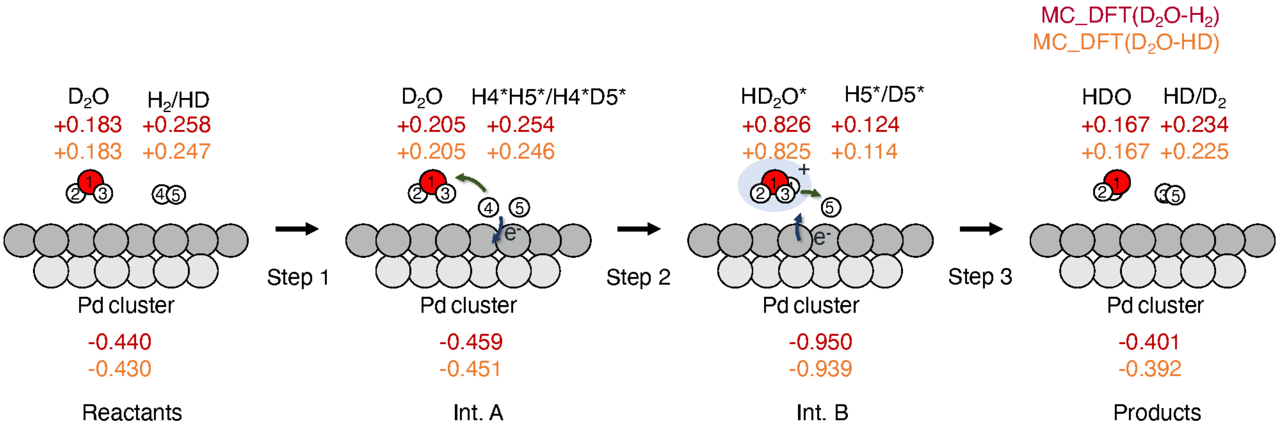


Fig. 4 Natural atomic charges of each structure group in the D_2O–H_2 and D_2O–HD systems obtained by NBO analysis.

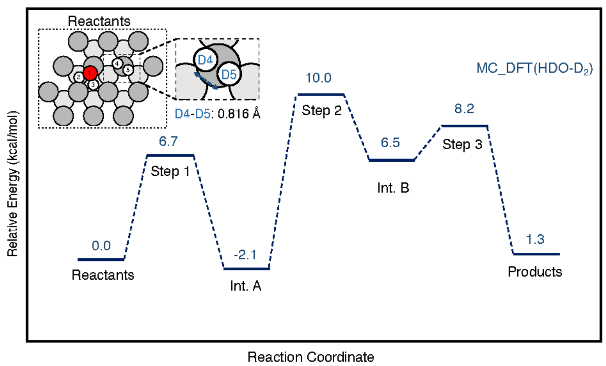


Fig. 5 Energy diagram of D/H exchange reaction between HDO and D_2 on a Pd surface obtained using the MC_DFT.

The activation energy for Step 1 in the HDO–D_2 system was 6.7 kcal/mol, which is 1.4 kcal/mol larger than that of the H/D exchange reactions in the D_2O–H_2 system (Fig. 3). Thus, D_2 bond dissociation was slower than H_2 bond dissociation. In addition, the MC_DFT calculations represent the H/D geometrical isotope effects. The D4–D5 bond length in the reactants was 0.816 Å, which is smaller than the H4–H5 bond length (0.837 Å) in the reactants of the D_2O–H_2 system (Fig. 3). Meanwhile, the activation energy for Step 2 was 12.1 kcal/mol, which is almost the same as for Step 2 in the D_2O–HD system. Thus, no notable H/D isotope effect on the activation energy for Step 2 was observed. The H/D isotope effect on the activation energy was observed only in the dissociation step (Step 1). Although the activation energy for Step 1 was less than that for Step 2, the H/D isotope effect on the activation energy for Step 1 might render the reaction of D_2 and HD more difficult than the reactions of H_2 and HD.

In conclusion, we analyzed the H_2/D_2 exchange reaction catalyzed by Pd/C using the MC_DFT to clarify the involved mechanism. Our results suggest that the Grotthuss mechanism, in which only the H_2 molecule underwent dissociative adsorption on the metal surface and an HD_2O^* was formed as an intermediate, was the most plausible. In addition, HD_2O^* was positively charged because of the charge transfer from the adsorbed molecules to the metal surface. MC_DFT calculations also revealed that the activation barrier for D_2 dissociation is higher than that for H_2 dissociation. Thus, the D/H exchange reaction from D_2 is less likely to occur. Overall, this study offers detailed insights into the H/D exchange reaction proposed by us[5] for the first time, providing crucial and fundamental knowledge for developing more efficient H/D exchange reactions.

Author contributions

T.U. designed the study and the main conceptual ideas. H.T. performed the calculation. T.U., and H.T. conducted the analysis for the calculation results. T.U., H.T., T.I., H.S. and M.T. aided in interpreting the results and worked on the manuscript. T.U., T.I, H.S. and M.T. supervised the project. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.

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Data availability

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The data supporting this article have been included as part of the ESI.