Toward Low-Temperature Dehydrogenation Catalysis: Isophorone Adsorbed on Pd(111)

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ABSTRACT: Adsorbate geometry and reaction dynamics play essential roles in catalytic processes at surfaces. Here we present a theoretical and experimental study for a model functional organic/metal interface: isophorone (C₉H₁₄O) adsorbed on the Pd(111) surface. Density functional theory calculations with the Perdew–Burke–Ernzerhoff (PBE) functional including van der Waals (vdW) interactions, in combination with infrared spectroscopy and temperature-programmed desorption (TPD) experiments, reveal the reaction pathway between the weakly chemisorbed reactant (C₉H₁₄O) and the strongly chemisorbed product (C₉H₁₀O), which occurs by the cleavage of four C–H bonds below 250 K. Analysis of the TPD spectrum is consistent with the relatively small magnitude of the activation barrier derived from PBE+vdW calculations, demonstrating the feasibility of low-temperature dehydrogenation.

Heterogeneous catalysis plays an essential role in the chemical processing industry for production of pharmaceuticals and clean energy technologies.¹ Conversion of unsaturated hydrocarbons on transition metals is of immense practical importance because it provides large-scale manufacturing of valuable intermediates for many chemical processes. These types of reactions were extensively investigated in the early years using conventional catalytic techniques¹–² and more recently by modern surface science methodologies.³–⁷ To design the next generation of heterogeneous catalysts, it is necessary to understand the adsorption and chemistry of molecules which are versatile enough to display complex functionality. Here we choose the adsorption of isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) on the Pd(111) surface as a prototypical model to study the mechanisms that govern the adsorption dynamics of organic/metal interfaces. Isophorone is an important proxy for catalysis because it contains conjugated C=C and C=O bonds that can be selectively hydrogenated. Isophorone is also a prochiral molecule that can be transformed to two enantiomers after selective hydrogenation of the olefinic double bond.⁸

Here we present density functional theory (DFT) calculations including van der Waals interactions (vdW), in combination with infrared (IR) spectroscopy and temperature-programmed desorption (TPD) experiments to reveal the reaction pathway from the weakly chemisorbed C₉H₁₄O reactant to the strongly chemisorbed C₉H₁₀O product after four C–H bond cleavages. Both the experimental TPD data and the relatively small magnitude of the activation barrier derived from DFT+vdW calculations support the feasibility of low-temperature dehydrogenation process. Our study illustrates the feasibility of understanding complex catalytic systems by using a combination of theoretical and experimental techniques. As shown in Figure 1, isophorone is an α,β-unsaturated cyclic ketone with a variety of functional groups: carbonyl, olefinic double bond, cyclohexene ring, lone methyl group, and twin methyl group. Figure 1 also shows the experimental IR spectrum of isophorone in the gas phase together with 0.3 monolayers (MLs) of isophorone adsorbed on Pd(111) measured at 130 K. The vibrational modes of the adsorbed molecule change significantly with respect to the gas phase. The most intense peak of the isophorone molecule in the gas phase, located at 1661 cm⁻¹, vanishes upon adsorption, whereas the bands associated with C–H stretching vibrations, located at 2700–3000 cm⁻¹, remain largely unperturbed. To understand the modification of the structure of the adsorbed isophorone molecule, we carry out DFT calculations using the FHI-aims all-electron code⁹ with the Perdew–Burke–Ernzerhof (PBE) functional.¹⁰ We find that vdW interactions are crucial for the correct description of isophorone adsorbed on Pd(111). For example, the most stable adsorption geometry and the dehydrogenation pathway can be obtained only by taking into account the vdW forces. Therefore, the PBE+vdW method¹¹ is employed for calculating dispersion interactions. The importance of including vdW interactions for organic molecules on metal surfaces has also been recently demonstrated in literature.¹²–¹⁴

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We explored the potential-energy surface (PES) of a single isophorone in a \((4 \times 4)\) supercell by varying the orientation and position of the molecule on top of Pd(111), followed by geometry relaxation. The uppermost two metal layers are allowed to relax, whereas the bottom layers are fixed at their bulk positions. Note that a very large supercell is not necessary for our calculations because the experiments are carried out at moderate coverages. All stable configurations correspond to the oxygen atom, forming a bond with a single Pd atom at the Pd(111) surface. This restricts the complexity of the PES and allows a systematic search for the possible adsorption configurations. We identified five minima that correspond to different tilting angles and lateral positions of isophorone on Pd(111). Figure 2 illustrates the two most stable adsorption structures (S–I and S–II) found in PBE+vdW geometry.
Owing to the higher stability of S−I, we computed the IR spectrum for this structure using the harmonic approximation (Figure 1, (Full)). The calculated spectrum reproduces the experimentally observed vanishing of carbonyl and C═C (or olefinic) stretching modes that is expected to occur for a flat-lying C═O and C═C bonds with respect to the substrate as a consequence of the metal−surface selection rule.17 However, there is no qualitative agreement between the calculated and the measured spectra in the high frequency 2200−2900 cm−1 region. The most visible difference appears at 2573 cm−1, corresponding to the stretch mode of C−H at site A. This discrepancy can arise from substantial broadening of this vibrational band due to a very short lifetime of the C−H−Pd bond precluding its experimental observation. Alternatively, isophorone can decompose by losing the H atom at site A. The latter scenario is very likely on Pd(111), which is known to be active for dehydrogenation reactions.15,18−20 Furthermore, no mass-spectrum signal corresponding to the intact isophorone molecule was observed in our TPD experiments at low coverage, clearly supporting the dehydrogenation scenario. To explore this possibility and explain the discrepancy between experiments and theory in the IR spectra, we proceed to eliminate the isophorone H atom closest to the Pd(111) substrate (position A in Figure 1). In the low and intermediate coverage limits, which also correspond to the experimental situation, dissociated hydrogen atoms can diffuse on the Pd(111) surface after dehydrogenation occurs, even at low temperatures. The small calculated H diffusion barrier on Pd(111) (0.12 eV, consistent with the literature21) confirms this hypothesis. We thus define the reaction enthalpy of the partially dehydrogenated isophorone molecule, $E_r$, as

$$E_r = E_{sys} + N \times E_{H/Pd(111)} - (N + 1) \times E_{Pd(111)} - E_{mol}$$ (1)

where $N$ denotes the number of the C−H bond cleavages. The reaction enthalpy is divided into four contributions: (i) the dehydrogenated isophorone on Pd(111), $E_{sys}$; (ii) a single H atom at the hollow site of Pd(111), $E_{H/Pd(111)}$; (iii) the clean Pd(111) surface, $E_{Pd(111)}$; and (iv) the intact isophorone molecule, $E_{mol}$. Following the first dehydrogenation at site A, we further sequentially remove the hydrogens closest to the substrate, up to five C−H bond cleavages. The calculated $E_r$ values as a function of the dehydrogenation step are shown in Figure 3. The inclusion of vdW interactions does not affect the calculated trend and results in an increase in the reaction enthalpy. During incremental dehydrogenation steps, the stability consistently increases from the full molecule adsorption (Full) to the fourth dehydrogenation step (A+B+C+D) and then decreases at the fifth step (A+B+C+D+E). We have considered three other possible sites for the fifth dehydrogenation, and none was more stable than site E. The relaxed geometry at the minimum enthalpy point (A+B+C+D) shows that the entire molecule is flat on the Pd(111) surface and that C−Pd bonds are formed due to the cleavage of the C−H bonds. Note that Figure 3 shows just one of the possible dehydrogenation sequences by “manual” elimination of the H atoms closest to the Pd(111) surface. However, our systematic calculations have confirmed that the fourth step − with these specific four hydrogen atoms extracted − always yields the minimum reaction enthalpy.

Figure 3. Calculated reaction enthalpy $E_r$ in electronvolts as a function of dehydrogenation step for isophorone/Pd(111). The PBE+vdWsurf approach includes the screening of the vdW energy in the Pd bulk.16 The adsorption structure at each step is also shown, where the carbon atom participating in the dehydrogenation is indicated in each plot. The geometry at the minimum enthalpy point (A+B+C+D) corresponds to a flat molecule on the surface.
The calculated vibrational spectra of the dehydrogenated systems are shown in Figure 1, from the first C–H bond cleavage (A) to the fourth (A+B+C+D). For the initial dehydrogenation, the extremely sharp IR peak, located at 2573 cm\(^{-1}\) in the full-molecule system, vanishes after the first C–H cleavage. However, two small peaks remain in the range of 2700–2900 cm\(^{-1}\), corresponding to the stretches of the C–H at sites B and C. After the second dehydrogenation step, as shown in Figure 1 (A+B), an intensive peak appears at 2772 cm\(^{-1}\) due to the stretch mode of the C–H bond at site C, which is not observed in the experimental spectrum. Further removing the third H at site C leads to a qualitative agreement with the experiments. The agreement remains the same after the fourth dehydrogenation step. We conclude based on the IR spectra that multiple (three to four) dehydrogenation steps occur. To gain better understanding of the dehydrogenation kinetics, we use TPD experiments and calculate activation barriers to probe how many C–H bonds break upon adsorption of isophorone on Pd(111).

Decomposition of isophorone was probed by TPD on Pd(111) in the temperature range 100–750 K under ultra-high-vacuum conditions. For isophorone coverages in the range of 0.3 to 0.6 ML, no molecular desorption of intact molecule was observed, suggesting complete dissociation of adsorbed species; see Figure 4 (bottom). The strongest signal of intact isophorone molecules (mass 138) is at mass 82, which results from decomposition in the quadrupole mass spectrometer. One of the most prominent desorbing species was H\(_2\), which results from isophorone dissociation (see Figure 4). Typically, four distinct desorption peaks at 320–350, 485, 570, and 620 K can be distinguished. Note that the onset of hydrogen desorption from Pd(111) is well-known to be around 300 K, which means that the first H\(_2\) peak is desorption/recombination-limited and that the early decomposition steps contributing to this peak may occur well below 300 K. All of the subsequent peaks can be undoubtedly attributed to stepwise decompositions at the corresponding temperatures. Assuming that dissociation of each isophorone molecule can release up to the full 14 H atoms, the number of H atoms released in each H\(_2\) desorption peak was quantified. Before the onset of H\(_2\) desorption at \(\sim 250\) K, four to six H atoms are produced on the surface depending on the ML coverage, where the number six corresponds to the low coverage of 0.3 ML. Because of the coverage used in our calculations (1 molecule per 16 surface atoms, \(\sim 0.5\) ML), the theoretical prediction of four C–H bond cleavages closely matches the TPD result at 0.6 ML. No other molecular decomposition products of isophorone were detected in our experiments at this temperature, which means that the H\(_2\) trace reflects stepwise decomposition of isophorone and not that of some other molecular surface species. Note that the onset temperature of H\(_2\) desorption is indicative of recombination of two surface hydrogen atoms,\(^{24}\) thus the formation of subsurface hydrogen species, which typically desorb from Pd in the range of 200–300 K,\(^{22–24}\) can be excluded.

To understand further the feasibility of low-temperature dehydrogenation, we proceed to calculate the barriers for the dehydrogenation reaction. The climbing image nudged elastic band (CI-NEB)\(^{25}\) method was used to determine the activation barrier for dissociation, \(E_a\). The transition state was characterized by identification of a single imaginary frequency, which corresponds to a saddle point on the PES. Different starting points have been considered for the first C–H cleavage, and site B is found to have the smallest \(E_a\) of 0.57 eV in PBE +vdW. This value is reduced to 0.36 eV after including the zero-point energy (ZPE), which is known to play an important role in dehydrogenation reactions.\(^{26,27}\) The vdW interactions also play a significant role in catalytic reactions.\(^{26}\) As exemplified in our system, the \(E_a\) value from PBE+vdW is \(\sim 0.1\) eV smaller than that from the PBE functional. An even smaller dehydrogenation barrier is found at site A for the second C–H cleavage. In this case, \(E_a\) is determined to be 0.43 eV without ZPE and reduces to 0.21 eV with ZPE correction. Our simulations agree with the previous conclusion that the first C–H cleavage is the rate-controlling step during a series of the dehydrogenation reactions.\(^{20}\)

The calculated barrier of 0.36 eV for isophorone decomposition corresponds to the temperature range from 130 to 150 K, as estimated by Redhead analysis\(^{29}\) for the range of preexponential factors \(10^{16}\) to \(10^{13}\) s\(^{-1}\), correspondingly, that is typical for large molecules adsorbed on transition metal surfaces.\(^{30–32}\) The estimated temperature range is in a good agreement with the experimentally observed decomposition below \(\sim 250\) K.

In conclusion, a joint theoretical and experimental study is carried out to investigate the structural, vibrational, and catalytic properties of isophorone on the Pd(111) surface. The most stable adsorption geometry can be clearly identified only after the vdW interactions are included in the DFT.
calculations. The calculated geometry is in an excellent agreement with the experimental IR spectra, suggesting a flat-lying configuration of the adsorbate. The reaction enthalpy correctly predicts a low-temperature dehydrogenation pathway from the weakly chemisorbed reactant (C_9H_{14}O) to the strongly chemisorbed partially dehydrogenated adsorbate (C_9H_{10}O). The cleavage of four C–H bonds predicted theoretically is consistent with the TPD results, showing that four to six H atoms can be stripped off below 250 K.

■ ASSOCIATED CONTENT

1 Supporting Information
Experimental details of isophorone adsorbed on the Pd(111) surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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