Effects of Hydrogen and Propylene Presence on Decomposition of Hydrogen Peroxide over Palladium Catalysts

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Abstract

Reaction rates for H_2O_2 decomposition in a methanol solution were measured over Pd/SiO_2 catalysts in the presence of gas-phase N_2 , H_2 and propylene. The H_2O_2 decomposition rates were higher in the presence of H_2 and lower in the presence of propylene compared to those under N_2 , which acted as an inert gas. For interpretation of the experimental results, H_2O_2 decomposition reactions were evaluated with density functional theory calculations on four $\text{Pd}(111)$ surfaces: (1) clean, (2) with pre-adsorbed hydrogen, (3) with molecularly pre-adsorbed propylene, and (4) with dissociatively pre-adsorbed propylene. The computational results show that the mechanism of H_2O_2 decomposition can proceed through O-O and O-H bond splitting reactions. The O-O bond splitting reactions are energetically preferable because they are exothermic and have lower activation energies. However, in the absence of H_2 , the endothermic O-H bond splitting reactions with higher activation energies are required for the formation of molecular decomposition products: O_2 and H_2O . In contrast, in the presence of H_2 , the O-H bond splitting reactions are no longer required, and the H_2O_2 decomposition can proceed only through the facile O-O bond splitting reaction in H_2O_2 . The formed surface OH species can readily react with H species from dissociative H_2 adsorption, forming H_2O as the only product. This change in the reaction mechanism from the O-H bond splitting to the O-O bond splitting explains the experimentally observed higher H_2O_2 decomposition rates in the presence of H_2 . The lower H_2O_2 decomposition rates in the presence of propylene are due to blocking of Pd surface sites by hydrocarbon species formed on propylene adsorption. Although propylene does not directly participate in H_2O_2 decomposition, it adsorbs on Pd more strongly than H_2O_2 and, therefore, forms surface spectator species that reduce the number of Pd active sites.

1. Introduction

Hydrogen peroxide, H_2O_2 , is an important chemical that is widely used as an environmentally-friendly oxidizing agent in numerous household and industrial applications. For example, it is used in the production of disinfectants and laundry detergents as well as for waste water treatment and for bleaching in the production of paper and textiles. Although the use of H_2O_2 is environmentally-friendly, its current production is based on a multistep anthraquinone process with consecutive hydrogenation and oxidation steps. Since this process requires at least two reactors, large recycle streams and multiple separation units, it is usually economical to operate only large-scale centralized plants. In addition, the concentration of H_2O_2 needs to be increased by distillation prior to its transportation from a production plant in order to reduce the transported volume and then diluted back to smaller concentrations prior to its local use. It is, therefore, desirable to develop an efficient simplified process for small-scale (less than 50,000 tons/year) local on-demand production of H_2O_2 directly from H_2 and O_2 [1-3].

One of the main challenges in the development of an economical process for the direct H_2O_2 synthesis is minimizing the side reactions that lead to wasteful water formation. The challenge is that Pd-based catalysts that are efficient in the direct H_2O_2 synthesis are also effective in catalyzing water formation from two side reactions: (1) directly from H_2 and O_2 and (2) from H_2O_2 decomposition in the presence of H_2 [1, 4]. The overall result from both reactions is wasteful H_2 burning to water. In order to deconvolute the reaction mechanism of water formation over Pd catalysts, it is useful to analyze separately the H_2O_2 decomposition in the presence of H_2 . This reaction is sometimes referred to as H_2O_2 reduction.

Previous studies of H_2O_2 decomposition compared reaction rates in the presence and absence of H_2 over 2 wt % Pd/ SiO_2 in a flow microreactor [5, 6], 5 wt % Pd/ Al_2O_3 in a batch reactor [7, 8] and 3 wt % Pd supported on an activated carbon cloth in a batch reactor [9].

These studies showed that the presence of H_2 significantly increased the decomposition rates. This effect was observed with different solvents and stabilizing agents under various experimental conditions. The higher rates in the presence of H_2 were tentatively assigned to an increase in the fraction of metallic Pd atoms. This explanation was proposed based on the observed slow deactivation of a 5 wt % Pd/C catalyst in consecutive H_2O_2 decomposition reaction runs in a batch reactor at 298 K [10]. The deactivation was attributed to gradual oxidation of the Pd surface by O_2 produced in H_2O_2 decomposition. The argument was that the presence of H_2 makes the Pd surface more metallic and, therefore, makes the catalyst more active. This explanation, however, is inconsistent with the results of H_2O_2 decomposition in the presence of flowing O_2 reported by the same group [7]. The H_2O_2 decomposition rates practically did not change over a 5 wt % Pd/ Al_2O_3 catalyst in a batch reactor at 300 K when the reaction was first conducted under flowing N_2 and then repeated under flowing O_2 [7]. Therefore, the presence of O_2 at the typical reaction conditions was not significant.

Furthermore, the reaction kinetics of H_2O_2 decomposition were reported to change over 2 wt % Pd/ SiO_2 at 303-323 K in the presence of H_2 [5, 6]. The apparent reaction orders in H_2O_2 at different temperatures were only positive in the absence H_2 [5]. In contrast, the apparent reaction orders in H_2O_2 changed from being positive, to zero and then to negative with increasing H_2O_2 concentrations in the presence of H_2 under the same reaction conditions [6]. These kinetic differences indicate that the reaction mechanism changes in the presence of H_2 .

In this work, reaction rates of H_2O_2 decomposition were systematically compared over oxidized and reduced Pd/ SiO_2 catalysts in the absence and presence of H_2 . Effects of H_2 presence on elementary reaction steps in H_2O_2 decomposition on Pd were analyzed at the molecular level with density functional theory (DFT) calculations. Our results identify how

the reaction mechanism changes in the presence of H_2 , explaining the experimental observations.

Due to its environmental friendliness, H_2O_2 is a desirable oxidizing agent for selective oxidation of hydrocarbons in the chemical industry. For example, it is advantageous to use H_2O_2 for selective oxidation of propylene to propylene oxide. Propylene oxide is used in the production of polyurethane plastics and multiple other large-volume commodity chemicals. The current production of propylene oxide is mostly based on either the multistep chlorohydrin process with salty waste streams and chlorinated byproducts or another multistep process with an aromatic hydrocarbon byproduct [11]. In order to improve the efficiency of propylene oxide production, The Dow Chemical Company and BASF have recently commercialized a new Hydrogen Peroxide – Propylene Oxide (HPPO) process, in which propylene oxide is produced by reacting H_2O_2 with propylene over a TS-1 catalyst in liquid phase [11-13]. In this process, unreacted H_2O_2 in the product stream needs to be decomposed in the presence of hydrocarbons. It is, therefore, useful to determine how the presence of propylene affects H_2O_2 decomposition over metals, such as Pd, that are active in catalyzing H_2O_2 decomposition. For example, effects of the reaction temperature and the solution pH on H_2O_2 decomposition in an HPPO product stream were experimentally evaluated over supported Pt and Pd catalysts with an objective of complete H_2O_2 decomposition [12].

A reverse objective, preventing wasteful H_2O_2 decomposition, is critically important in the development of a single-step process where in situ formation of H_2O_2 or surface OOH species can be combined with their immediate use for selective propylene oxidation in the same reaction mixture. Such a process with H_2 , O_2 and propylene as the feed and propylene oxide and H_2O as products is extensively studied as a gas-phase reaction over Au/TiO₂ and Au/TS-1 catalysts [11, 14]. For example, our recent study showed that an Au/Ti-SiO₂ catalyst can be

used with a membrane, with propylene and O_2 being forced through the catalytic membrane and H_2 reaching the catalyst by counter-diffusion [15]. Alternatively, a membrane reactor can produce H_2O_2 from H_2 and O_2 over Pd/SiO₂ in the first catalytic layer and then immediately utilize the produced H_2O_2 for selective hydrocarbon oxidation over TS-1 in the second catalytic layer [16]. Since such single-step processes in effect combine the direct H_2O_2 synthesis with propylene epoxidation, here it is also useful to determine effects of propylene presence on H_2O_2 decomposition over catalytic metals, including Pd, that are active in catalyzing H_2O_2 formation.

In this work, in addition to the evaluation of H_2 presence effects, reaction rates of H_2O_2 decomposition were systematically compared over oxidized and reduced Pd/SiO₂ catalysts in the absence and presence of propylene. The experimental results were analyzed with DFT calculations by comparing elementary reaction steps in H_2O_2 decomposition on a clean Pd surface and on Pd surfaces with pre-adsorbed hydrogen and propylene.

2. Experimental and computational methods

2.1. Catalyst Preparation

2 wt % Pd/SiO₂ catalysts were prepared using incipient wetness impregnation with palladium acetate (99.9%, Sigma Aldrich) and Davisil 643 silica (pore size 15 nm, 200-425 mesh, Sigma Aldrich). Prior to the Pd deposition, the SiO₂ support was dried at 373 K overnight. After the Pd deposition, the samples were first dried in vacuum at 393 K for 12 h and then calcined in air at 573 K for 4 h. After the calcination, the samples were split into two sets. The first set was tested without any additional pretreatment (oxidized Pd/SiO₂). The second set was tested after a reduction pretreatment in 10 mol % H_2 /He (99.999%, Linde grade 5.0) at a flow rate of ~20 sccm at 473 K for 2 h (reduced Pd/SiO₂).

The sizes of Pd nanoparticles in the oxidized and reduced samples were analyzed using multiple images, which were obtained with a FEI Tecnai G2 Sphera transmission electron microscope (TEM) at an acceleration voltage of 200 kV. Representative TEM images are shown in Figure 1. The histograms of particle size distributions for the oxidized and reduced Pd nanoparticles, which are also shown in Figure 1, demonstrate that, as expected for the conversion of an oxide to the metal, the size of nanoparticles decreased from 2.8 ± 0.6 nm for the oxidized Pd (Figure 1b) to 2.2 ± 0.6 nm for the reduced Pd (Figure 1a). Importantly, the particle size distributions indicate that the H_2 treatment did not cause any significant size changes for the Pd nanoparticles, only their reduction.

2.2. Catalyst Testing

Rates of H_2O_2 decomposition in a methanol solution were measured using a 100 ml glass autoclave batch reactor immersed in a cooling bath for temperature control. The autoclave had an internal thermocouple, pressure sensor and gas dispersion impeller. The temperature was kept constant at 313 K. The initial total pressure in the reactor was 6 bar. The reactor pressure varied slightly during the reaction due to O_2 evolution or H_2 consumption. In each test, 50 ml of an H_2O_2 methanol solution and 20 mg of a fresh 2 wt % Pd/SiO₂ catalyst were stirred continuously with the impeller at 700 rpm. The reaction was run in the presence of either N_2 (99.999%, Linde grade 5.0), which acted as an inert gas, 50 mol % H_2/N_2 (99.999%, Linde grade 5.0) or 50 mol % C_3H_6/N_2 (99.95%, Liner grade 3.5). For safety reasons, the initial H_2O_2 concentration (30 wt % with an inhibitor, Sigma-Aldrich product H3410) was reduced to 0.09-0.11 wt % in all experiments by diluting with methanol (99.8 wt %, VWR HPLC grade). This low initial concentration decreased the amount of any produced O_2 and, thus, allowed us to avoid explosive mixtures by ensuring an excess of either H_2 or C_3H_6 in the reactor. Changes in the H_2O_2 concentration were monitored at regular intervals by collecting

liquid samples, which were analyzed using the titration method with a Ce(IV) sulfate solution (0.05 M Ce(SO₄)₂, volumetric, Sigma Aldrich product 34253).

2.3. Density Functional Theory (DFT) Calculations

Adsorption of H₂O₂, H₂ and C₃H₆ as well H₂O₂ decomposition reactions on Pd surfaces were examined with periodic unit-cell DFT calculations using the DMol³ code in Materials Studio 4.0 software by BIOVIA Corp. Except for propylene, only the most stable adsorption configurations are reported. For propylene, both molecular and dissociative adsorption modes are reported. In the molecular mode, CH₂=CH-CH₃ binds to the surface through its C=C double bond without decomposition or rearrangement and forms di-σ-bonded species (Figure 2a). In the dissociative mode, one H atom from the CH₂ group splits off and adsorbs on the surface, the remaining second H atom transfers to the middle C atom, forming the propylidyne surface species (≡C-CH₂-CH₃* + H*, Figure 2b). Reaction and activation energies for H₂O₂ decomposition were calculated on four Pd(111) surfaces: (1) clean, (2) with pre-adsorbed hydrogen as 2H*, (3) with dissociatively pre-adsorbed propylene as C₃H₅* propylidyne and H* atomic hydrogen species, and (4) with molecularly pre-adsorbed propylene as di-σ-bonded C₃H₆* species.

Adsorption energies were calculated at 0 K without zero-point energy corrections using as a reference the sum of energies for the corresponding surface and isolated adsorbate molecule calculated separately. Reaction energies were calculated as energy differences for the products and reactants. Transition state searches for the O-O and O-H bond splitting reactions for adsorbed H₂O₂ were performed in three stages. In the first stage, calculations with constrained optimization were performed by gradually increasing the HO-OH and HOO-H bond distances. In the second stage, similar calculations with constrained optimization were performed for the reverse reactions by gradually decreasing distances between two OH surface species and between HOO and H surface species. In the third stage, the energetically

preferable reaction pathways identified with the constrained optimization calculations were confirmed and refined using a combination of linear synchronous transit (LST) and quadratic synchronous transit (QST) algorithms with conjugate gradient refinement.

The calculations used the double numerical with polarization (DNP) basis set and the generalized gradient-corrected Perdew-Wang (GGA PW-91) functional. Tightly bound core electrons for Pd were represented with semi-core pseudopotentials. Reciprocal-space integration over the Brillouin zone was approximated through k-point sampling with a separation of 0.5 nm^{-1} using the Monkhorst-Pack grid: $(3 \times 3 \times 1)$. Convergence with respect to the number of k-points was tested by increasing their number for representative structures. The density mixing fraction of 0.1 with direct inversion in the iterative subspace (DIIS) and orbital occupancy with thermal smearing of 0.002 Ha were used. The orbital cut off distance of 0.4 nm was set for all atoms. The surface of metallic Pd nanoparticles was modelled as an infinite Pd(111) surface constructed with a $3 \times 3 \times 5$ periodic unit cell, similarly to our previously reported Pt(111) models [17, 18]. The unit cell had 3×3 surface Pd atoms and 5 layers with a total of 45 Pd atoms. The full unit cell with adsorbed propylene is shown in Figure 2.

The first three top layers of the Pd(111) unit cell were relaxed and optimized with adsorbates during geometry optimizations, simulating surface relaxation after adsorption. The remaining two bottom layers were constrained at the bulk Pd crystal positions, simulating multilayer nanoparticles. The unit cell was generated from the bulk crystal using the optimized Pd lattice constant of 0.3976 nm with a vacuum spacing of 3 nm in the c direction.

3. Results

3.1. Experimental Kinetic Measurements

Prior to the catalyst testing, a blank run was conducted at the standard reaction conditions under N_2 but with only the SiO_2 support, instead of a Pd/SiO_2 catalyst. Liquid product samples in this run were collected and analyzed every 30 min. No detectable H_2O_2 decomposition was observed after 150 min of time on stream. This blank run demonstrated that the rate of H_2O_2 decomposition was negligible in the employed reactor system in the absence of Pd. Therefore, the measured H_2O_2 decomposition rates in the presence of the Pd/SiO_2 catalysts can be attributed exclusively to H_2O_2 reactions on Pd.

A comparison of testing results for the reduced (metallic) Pd/SiO_2 catalyst in the presence of N_2 , H_2 and C_3H_6 are presented in Figure 3a. Under N_2 , 91% of H_2O_2 decomposed after 60 min of time on stream (Table 1), and it took 83 min to reach 100% conversion. The conversion values at 60 min of time on stream in Table 1 were calculated using linear interpolation between two experimental values: one before and another after 60 min. Under H_2 , the decomposition rate increased, and all H_2O_2 decomposed in only 33 min. Under C_3H_6 , the decomposition rate decreased, and the conversion was only 68% after 60 min compared to 91% under N_2 (Table 1). It took more than twice as long, 143 min, to reach a similar conversion of 90% under C_3H_6 .

The testing results for the oxidized Pd/SiO_2 catalyst in the presence of N_2 , H_2 and C_3H_6 are presented in Figure 3b. The oxidized catalyst after 4 h of calcination in air at 573 K likely had a mixture of PdO and metallic Pd phases, with the surface being predominantly PdO . For comparison, changing the calcination temperatures from 408 to 508 K while keeping the duration at 12 h for catalysts with 3 wt % Pd supported on an activated carbon cloth produced samples with a fraction Pd atoms in the PdO phase ranging from 5 to 69%, based on X-ray photoelectron spectroscopic (XPS) measurements [9]. Surface science studies on the interaction of O_2 with $Pd(111)$ and other Pd single-crystal surfaces showed that the formation of a bulk PdO was limited by oxygen diffusion in Pd metal with an activation energy of 60–

85 kJ/mol and, after the formation of a PdO surface layer, by even slower oxygen diffusion in PdO with an activation energy of 111–116 kJ/mol [19].

The effect of switching from N₂ to H₂ for the oxidized catalyst remained the same: the H₂O₂ decomposition rate increased. The increase, however, was even more significant for the oxidized Pd/SiO₂ catalyst. Under N₂, 31% of H₂O₂ decomposed after 60 min (Table 1), and the conversion was still below 40% after 200 min. Under H₂, it took only 33 min to reach 100% conversion. The effect of switching from N₂ to C₃H₆ for the oxidized catalyst was different than the reaction rate decrease observed for the reduced catalyst. Initially, the decomposition rate under C₃H₆ was similar to that under N₂. After 60 min, the conversion was 33% under C₃H₆ and 31% under N₂ (Table 1). However, with additional time on stream, the conversion under C₃H₆ became slightly higher. After 168 min, the conversion was 42% under C₃H₆ and 33% under N₂.

The results shown in Figure 3 are presented in Figure 4 as a comparison between the oxidized and reduced Pd/SiO₂ catalysts. Under N₂, the decomposition rate was significantly lower for the oxidized Pd. The conversion was only 31% compared to 91% for the reduced Pd after 60 min (Table 1, Figure 4a). Under C₃H₆, the oxidized Pd was similarly less active, but the difference in the decomposition rates was less significant. The conversion was 33% for the oxidized catalyst compared to 68% for the reduced after 60 min (Table 1, Figure 4c). The activity difference was even less pronounced under H₂ (Figure 4b). Although the oxidized catalyst was initially less active, 100% conversion was observed for both catalysts after 33 min (Table 1, Figure 4b).

3.2. Computational Results

First, adsorption species for hydrogen and propylene on Pd(111) were calculated in order to generate surfaces for examining the mechanism of H₂O₂ decomposition in the presence of these molecules. The energies for dissociative hydrogen adsorption,

were similar on atop, bridge and three-fold Pd surface sites, with a slight preference for three-fold sites. The energetic preference of fcc three-fold sites on Pd(111) is in agreement with multiple previous computational studies, for example [20, 21]. The calculated adsorption energy for fcc three-fold sites was -108 kJ/mol. This value is in agreement with experimental measurements. Energies of -102 and -87 kJ/mol for adsorption on respectively Pd(110) and Pd(111) were reported for surface coverage values up to half a monolayer based on temperature programmed desorption (TPD) measurements [22]. Similar adsorption energies of -104 kJ/mol at low coverage were reported for Pd/SiO₂ based on microcalorimetric measurements [23].

For molecular propylene adsorption,

the preferred site was a Pd-Pd bridge with the formation of a di- σ -bonded configuration (Figure 2a). For dissociative propylene adsorption,

the preferred sites for both propylidyne (C-CH₂-CH₃) and atomic hydrogen adsorption were Pd three-fold sites (Figure 2b). The calculated adsorption energy of -148 kJ/mol was lower (greater stability) than -116 kJ/mol for the molecular adsorption mode. Both molecular and dissociative adsorption modes were evaluated because previous studies with TPD and reflection-absorption infrared spectroscopic (RAIRS) measurements [24] showed that propylene adsorbed on Pd(111) molecularly as mostly di- σ -bonded species at low temperatures and then transformed at ~300 K to mostly propylidyne species, which remained stable up to 550 K. Therefore, at our experimental temperature of 313 K, it is likely that both di- σ -bonded propylene and propylidyne species were present on Pd. The desorption energy for molecularly adsorbed propylene on Pd(111) was previously estimated at 79 kJ/mol in the

range of 270-390 K using laser-induced thermal desorption coupled with Fourier transform mass spectrometry (LITD/FTMS) measurements at high surface coverage conditions [25]. Our adsorption energy for the di- σ -bonded propylene of -116 kJ/mol was calculated at a low coverage value of 1/9 ML (1 hydrocarbon molecule on the 3 $\times$ 3 Pd unit cell surface, Figure 2a). Therefore, our calculated value at low coverage is likely lower (higher stability) than the value obtained based on the experimental measurements at high coverage due to destabilization of di- σ -bonded species by neighboring adsorbates with increasing coverage as well as the possible presence of less stable π -bonded species in the experimental measurements. Since direct measurements of heats of adsorption for propylene on Pd have not been reported, it is useful to compare the calculated values to reported measurements for ethylene. Our calculated value of -116 kJ/mol is consistent with the values from -110 to -102 kJ/mol reported for the initial heats of adsorption (low coverage conditions) for ethylene adsorption on Pd/SiO₂ at temperatures below 273 K with the formation of a mixture of di- σ and π -bonded species, based on microcalorimetric and IR spectroscopic measurements [26]. Similarly, our calculated value of -148 kJ/mol for propylidyne formation is consistent with the values reported for the initial heats of ethylene adsorption on Pd/SiO₂ at room temperature with the formation of a mixture of ethylidyne, di- σ and π -bonded species [23, 26]. The calorimetric heats of adsorption for ethylene at room temperature increased rapidly from the initial values of -170 – -160 to about -120 kJ/mol with increasing coverage and then exhibited an apparent minimum due to evolution of gas-phase ethane produced by a reaction of molecularly adsorbed ethylene with the surface hydrogen formed due to ethylidyne formation [23, 26].

After calculating the surface species for hydrogen and propylene, energies for adsorption and decomposition reactions of H₂O₂ (Figures 5 and 6) were evaluated on four surfaces: (1) clean Pd(111) (Figure 7), (2) Pd(111) with hydrogen atoms adsorbed on fcc three-fold sites

(Figure 8a), (3) Pd(111) with dissociatively adsorbed propylene as propylidyne and atomic hydrogen on fcc three-fold sites (Figure 8b), and (4) Pd(111) with molecularly adsorbed propylene as di- σ -bonded species on a bridge site (Figure 8c). In Figures 7 and 8, only the first two top layers of the Pd surface model are shown for clarity. The adsorption and reaction energies are summarized in Table 2.

For H₂O₂ molecular adsorption,

the preferential adsorption site was a single Pd atom with bonding through one of the oxygen atoms in an atop-bonded configuration (Figure 5a). The preferential adsorption sites and geometries for H₂O₂ and the surface species formed in H₂O₂ decomposition (OOH, OO and OH), described below, are in agreement with previous computational studies [20, 21].

The adsorption energy on the clean Pd surface (Figure 7a) was -55 kJ/mol. The adsorption energy was not significantly affected, and it remained at -55 kJ/mol (Table 2) in the presence of hydrogen (Figure 8a) and molecular propylene (Figure 8c). In the presence of dissociatively adsorbed propylene (Figure 8b), the adsorption energy was less negative (lower stability) at -41 kJ/mol due to repulsive interactions between the adsorbates.

There are only two possible reactions for the start of H₂O₂ decomposition on a clean Pd surface: either (1) splitting the O-O bond (Figure 5b) or (2) splitting one of the O-H bonds (Figure 5c). Transition states and reaction energies for these two reactions were evaluated in the absence and presence of hydrogen and propylene. In addition, reaction energies were evaluated for splitting the second O-H bond (Figure 5d).

The first reaction, the O-O bond splitting,

generates two surface hydroxyl groups (Figure 5b). The identified preferential reaction pathway on the clean Pd surface is illustrated in Figure 6a. Initially, the O atom, which was

not bonded to the surface, began approaching the neighboring Pd atom below it, and simultaneously the H atom, which was bonded to this O atom, started moving to a side of the H₂O₂ molecule (Figure 6a-II). The side movement of the H atom allowed the O atom to establish a bond with the Pd atom with increasing O-O bond distance. In the transition state (Figure 6a-III), the O-O bond distance increased from 0.148 nm in the adsorbed H₂O₂ to 0.161 nm, and the molecule formed a Pd-O-O-Pd cycle. The activation energy was 10 kJ/mol, in agreement with values of 4–22 kJ/mol reported in previous DFT studies [20, 21, 27]. The OH fragments pointed in opposite directions (trans configuration). The cis configuration was less energetically favorable. After the transition state, the two formed OH species in the trans configuration continued moving away from each other (Figure 6a-IV). At an increased separation distance, however, it became energetically preferable for one of the OH species to rotate into a cis configuration in order to establish a hydrogen bond with the second OH species. In the product configuration, the two OH species were in the cis configuration on neighboring Pd-Pd bridge sites without sharing Pd atoms with an O-O separation distance of 0.283 nm (Figure 6a-V). This reaction was highly exothermic (thermodynamically favorable) on all the evaluated surfaces (Table 2): from -196 kJ/mol on the clean Pd(111) (Figure 7b) to -164 kJ/mol in the presence of dissociatively adsorbed propylene (Figure 8b). The preferred adsorption site for OH species was a Pd-Pd bridge (Figure 6b). The changes in the reaction energies, similarly to the changes in the H₂O₂ adsorption energies, were caused by adsorbate-adsorbate interactions, which increased with increasing surface coverage due to the formation of the decomposition products. The same trend was observed for the activation energies. However, the activation energies were affected less than the reaction energies because the transition states were intermediate geometries in the formation of the decomposition products. The activation energy remained at 10 kJ/mol in the presence of adsorbed hydrogen

and increased to 12 and 15 kJ/mol in the presence of, respectively, molecularly and dissociatively adsorbed propylene (Table 2).

The second reaction, the O-H bond splitting,

generates surface hydroperoxy and atomic hydrogen species (Figure 5c). The identified preferential reaction pathway on the clean Pd surface is illustrated in Figure 6b. It was energetically preferable to split off the H atom from the O atom, which was not bound to Pd. Initially, the H_2O_2 molecule rotated into a three-fold site (Figure 6b-II). Similarly to the O-O bond splitting in Figure 6a, the O atom, which was not bonded to the surface, began approaching the neighboring Pd atom below it, and simultaneously the H atom, which was bonded to this O atom, started moving to a side of the H_2O_2 molecule. However for the O-H bond splitting reaction, the cis configuration, with both H atoms being on the same side of the H_2O_2 molecule, was energetically preferable. In the transition state (Figure 6b-III), the initially bonded O atom remained bonded to one of the Pd atoms of the three-fold site while the second O atom became bonded to the second Pd atom, allowing the reacting H atom to establish a bond with the third Pd atom of this three-fold site. The O-H bond distance increased from 0.100 nm in the adsorbed H_2O_2 to 0.155 nm in the transitions state. After the transition, the reacting H atom moved to a neighboring three-fold site, and the OOH species remained on the bridge site with bonding through both O atoms (Figure 6b-IV). The presence of a neighboring surface H atom, however, made the OOH species unstable on its original bridge site and caused this fragment to rotate first to a neighboring three-fold site and, finally, to a bridge site that did not have shared bonding Pd atoms with the surface H atom (Figure 6b-V). Alternatively, the surface H atom could move further away from the OOH species on its original Pd bridge site, generating a configuration that was identical to the final structure in Figure 6b-V. The activation energy was 70 kJ/mol, in agreement with values of 63-79

kJ/mol reported in previous DFT studies [20, 21, 28]. Importantly this value was considerably higher than 10 kJ/mol for the O-O bond splitting reaction. Furthermore, in contrast with the O-O bond splitting, the O-H bond splitting reaction was endothermic (thermodynamically unfavorable) on all the surfaces (Table 2): from 8 kJ/mol on the clean Pd(111) (Figure 7c) to 16 kJ/mol in the presence of molecularly adsorbed propylene (Figure 8c), to 22 kJ/mol in the presence of adsorbed hydrogen (Figure 8a) and 41 kJ/mol in the presence of dissociatively adsorbed propylene (Figure 8b). The preferred adsorption site for OOH species was a Pd-Pd bridge (Figure 7c). The activation energies were affected less than the reaction energies and increased to 75 kJ/mol in the presence of adsorbed hydrogen and molecular propylene and 88 kJ/mol in the presence of dissociatively adsorbed propylene (Table 2). However, the activation energy increases for the O-H bond splitting reaction due to the coverage effects (from 70 to 88 kJ/mol) were higher than those for the O-O bond splitting reaction (from 10 to 15 kJ/mol). As a result, the O-O bond splitting reaction remained considerably more energetically preferable.

The splitting of the second O-H bond,

with the formation of adsorbed molecular oxygen and atomic hydrogen species (Figure 5d), similarly to the splitting of the first O-H bond, was endothermic on all the surfaces: from 12 kJ/mol on the clean Pd(111) (Figure 7d) and in the presence of molecularly adsorbed propylene (Figure 8c) to 24 kJ/mol in the presence of adsorbed hydrogen (Figure 8a) and 27 kJ/mol in the presence of dissociatively adsorbed propylene (Figure 8b). The preferred adsorption site for molecular oxygen species was an fcc three-fold site (Figure 7d).

4. Discussion

4.1. Decomposition mechanism through O-H bond splitting (in the absence of H_2)

Out of the two initial reactions in H_2O_2 decomposition: (1) the O-O bond splitting and (2) the O-H bond splitting, the first reaction with the formation of two OH species (Figures 5b and 6a) is predicted to have a low activation energy of 10-15 kJ/mol, regardless of the surface coverage, and remain highly exothermic with reaction energies from -196 to -164 kJ/mol (Table 2). Even though the O-O bond splitting is expected to be energetically preferable under all conditions, this reaction by itself does not lead to the formation of any molecular decomposition products in the absence of gas-phase H_2 . This reaction is limited only to the formation of highly stable surface hydroxyl species. Formation of any molecular decomposition products requires splitting of at least one of the O-H bonds.

In contrast with the O-O bond splitting reaction, the O-H bond splitting reaction in H_2O_2 with the formation of OOH and H surface species (Figures 5c and 6b) is predicted to have a higher activation energy of 70-88 kJ/mol, regardless of the surface coverage, and remain endothermic with reaction energies of 8-41 kJ/mol (Table 2). However, since this is a required reaction, the mechanism of H_2O_2 decomposition must proceed through the O-H bond splitting as the rate determining step.

After the formation of OOH species, the splitting of the second O-H bond with the formation of surface O_2 and H species (Figure 5d) is also predicted to be endothermic (Table 2). The activation energies of 57–78 kJ/mol reported for this reaction in previous DFT studies [21, 28] are similar to those for the splitting of the first O-H bond in H_2O_2 .

The O-H splitting reactions can be assisted by surface OH species, so that these reactions become $\text{HOOH}^* + \text{OH}^* = \text{OOH}^* + \text{H}_2\text{O}^*$ and $\text{OOH}^* + \text{OH}^* = \text{OO}^* + \text{H}_2\text{O}^*$. They can also be assisted by hydration and other solvation effects. However, the O-H bond splitting reactions are likely to remain less energetically preferable than the O-O bond splitting and, therefore, to remain rate limiting.

Another possible O-H bond splitting reaction is the disproportionation of surface OH species: $2\text{OH}^* = \text{O}^* + \text{H}_2\text{O}^*$. If the reaction mechanism proceeded through the OH disproportionation instead of the O-H bond splitting in HOOH and OOH, the gas-phase O_2 product would be formed by atomic oxygen surface species. In this case, oxygen isotope scrambling would be expected for a mixture of $\text{H}_2^{16}\text{O}_2$ and $\text{H}_2^{18}\text{O}_2$ with the formation of gas-phase $^{16}\text{O}^{18}\text{O}$. In contrast, if the reaction mechanism proceeds mostly through the O-H bond splitting in HOOH and OOH, the gas-phase O_2 product is formed not by atomic, but by molecular O_2 surface species, and isotope scrambling is not expected. Only $^{16}\text{O}_2$ and $^{18}\text{O}_2$ gas-phase products should be formed. Although such isotope experiments have not been reported for Pd, there are two studies published in 1952 that evaluated isotope effects in H_2O_2 aqueous solutions for other catalysts [29, 30]. These studies suggest that all the produced gas-phase O_2 comes exclusively from H_2O_2 , not from water, and, therefore, water does not directly participate in H_2O_2 decomposition. Since water can produce surface OH species, this result provides some evidence against the OH disproportionation. In addition, only limited oxygen isotope scrambling was reported for MnO_2 , Fe_2O_3 , colloidal Au and metallic Pt [30]. Future oxygen isotope studies for Pd should be able to clarify the reaction mechanism.

In the presence of methanol as a solvent, methoxy OCH_3 surface species are expected to form on Pd through dissociative adsorption. The formation of methoxy species and other solvent effects were not considered in this study because, as mentioned in the Introduction, the effects of H_2 presence on the rate of H_2O_2 decomposition were previously consistently observed with different solvents and stabilizers under various experimental conditions.

The formation of a Pd hydride phase in the presence of H_2 was not considered in this study because only a limited amount of $\beta\text{-PdH}_x$ was expected due to the small size of Pd particles in our catalysts (2.2 nm). The hydrogen solubility in Pd was found to decrease with decreasing

size of Pd particles [31, 32]. Specifically, the stoichiometry of β -PdH_x was found to decrease from $x=0.72$ for a Pd bulk [31] to 0.03 for 2 nm Pd particles supported on SiO₂ [32].

The combination of the O-O bond splitting reaction (Figure 5b) for one H₂O₂ molecule and the O-H bond splitting reactions for another H₂O₂ molecule (Figures 5c,d) allows the formation of molecular oxygen and water as the decomposition products since the OH and H surface species can readily react to produce water. The overall reaction in Figure 5, therefore, is $2\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}_2\text{O}$.

In summary, in the absence of gas-phase H₂, the mechanism of H₂O₂ decomposition must include an O-H bond splitting reaction, which has a high activation energy and, therefore, becomes the rate determining step. A combination of O-O bond splitting reactions, which are facile, with O-H bond splitting reactions, which have higher activation energies, leads to the formation of O₂ and H₂O as the reaction products.

4.2. Decomposition mechanism through O-O bond splitting (in the presence of H₂)

Gas-phase H₂ readily adsorbs and dissociates on Pd surfaces. This is evidenced, for example, by facile H₂ and D₂ isotope exchange reactions. A low activation energy of ~25 kJ/mol was reported for the H₂ + PdD and D₂ + PdH exchange reactions for Pd powders, based on kinetic measurements in a batch reactor at 178–323 K [33]. In addition, DFT calculations indicate that the dissociative H₂ adsorption on Pd(111) has an activation energy of close to zero [20, 27].

Therefore, in the presence of gas-phase H₂, the O-O bond splitting reaction is sufficient in the decomposition of H₂O₂ because the formed OH groups can readily react with surface H species from gas-phase H₂ and produce water as the decomposition product. The activation energy for this reaction, $\text{OH}^* + \text{H}^* = \text{H}_2\text{O}^* + *$, was estimated at 38–41 kJ/mol, based on DFT calculations [20, 21]. The overall reaction, thus, becomes $\text{H}_2\text{O}_2 + \text{H}_2 = 2\text{H}_2\text{O}$. Importantly, the endothermic O-H bond splitting reactions with high activation energies are

no longer required in this case. As a result of this change in the reaction mechanism, the rate of H_2O_2 decomposition increases significantly in the presence of H_2 (Figure 3).

This change in the reaction mechanism also explains the experimentally observed differences in the apparent reaction orders in H_2O_2 [5, 6], mentioned in the Introduction. In the absence of H_2 , the decomposition rate is controlled by the O-H bond splitting reactions, and the apparent reaction orders in H_2O_2 are expected to be only positive when the surface is dominated by OH species. In contrast, in the presence of H_2 when the reaction between OH and H surface species becomes rate limiting, the strongly-bound OH species formed through the O-O bond splitting in H_2O_2 inhibit H_2 adsorption and, in addition, inhibit further increases in the OH surface coverage to a greater extent compared to the changes in the H_2O_2 surface coverage and, therefore, decrease the H_2O_2 decomposition rate more strongly. Consequently, the apparent reactions orders in H_2O_2 change from being positive, to zero and then to negative with increasing H_2O_2 concentrations.

In summary, in the presence of gas-phase H_2 , the mechanism of H_2O_2 decomposition can proceed through the facile O-O bond splitting. The O-H bond splitting reactions, which have higher activation energies, are not required in this case because the formed OH surface species can react with H species from the dissociative H_2 adsorption. This change in the reaction mechanism from the O-H bond splitting to O-O bond splitting explains the experimentally observed higher reaction rates and the formation of H_2O as the only reaction product.

4.3. Effect of propylene presence

Propylene adsorbs on Pd more strongly than H_2O_2 . The heats of propylene adsorption of -116 kJ/mol for the di- σ -bonded species (Figure 2a, Reaction 2) and -148 kJ/mol for the propylidyne and atomic hydrogen species (Figure 2b, Reaction 3) are lower than the values from -55 to -41 kJ/mol for H_2O_2 adsorption (Figure 5a, Table 2, Reaction 4). The

hydrocarbon species formed by propylene adsorption do not directly participate in H_2O_2 decomposition. They act only as spectator species because no measureable amounts of hydrocarbon reaction products were detected at our experimental conditions for the reduced Pd/SiO₂ catalyst. The hydrocarbon spectator species, however, influence H_2O_2 decomposition indirectly by blocking Pd surface sites and, therefore, decreasing the number of Pd sites available for H_2O_2 adsorption and reactions. Such blocking of Pd active sites due to the stability of the hydrocarbon species provides an explanation for the lower rates of H_2O_2 decomposition in the presence of propylene compared to those under N_2 for the reduced catalyst in Figure 3a. The effect of site blocking in this case is more significant than any possible reactions with surface H species produced in the formation of propylidyne species (Figure 2b, Reaction 3).

In contrast, on an oxidized Pd surface, propylene cannot form strongly-bound di- σ -bonded or propylidyne species because they require, respectively, two or three adjacent Pd atoms (Figure 2). Since Pd atoms on an oxidized surface are surrounded by lattice O atoms, propylene can form only weakly bound π -bonded species on individual Pd atoms or react with lattice O atoms. The results in Figure 3b suggest that both adsorption and reactions with the surface must be taking place. Initially, adsorption and reaction effects counterbalance each other, and the H_2O_2 conversion values are similar under N_2 and propylene. On one hand, propylene adsorbs on Pd sites and blocks them from being active sites in H_2O_2 decomposition, decreasing the H_2O_2 decomposition rate. On the other hand, propylene reacts with lattice oxygen, makes the surface more metallic and, therefore, generates additional Pd active sites, increasing the rate of H_2O_2 decomposition. With time on stream, the conversion values in the presence of propylene become higher than those under N_2 (Figure 3b). Therefore, the effect of propylene surface reactions must be becoming more significant than the effect of site blocking by adsorption.

4.4. Effect of Pd oxidation

The lower H_2O_2 decomposition activity under N_2 for the oxidized catalyst with the expected PdO surface compared to that of the reduced catalyst with the expected metallic surface in Figure 4a is consistent with results of previous studies, which evaluated effects of Pd oxidation with and without different acid stabilizers in aqueous solutions [8, 10]. The lower activity of oxidized Pd can be attributed in part to a lower number (lower surface density) of Pd sites on oxidized surfaces. In addition, the lower activity may be due to inherently lower activity of electropositive Pd atoms (electronic effect) and to the fact that surface Pd atoms are surrounded by lattice O atoms (geometric effect).

The difference in activities for the oxidized and reduced catalysts becomes smaller in the presence of propylene (Figure 4c and Table 1). As mentioned above, this can be attributed to reactions between propylene and surface lattice oxygen, leading to gradual reduction of the Pd surface and, consequently, to increasing activity with time on stream. And finally, in the presence of H_2 , the oxidized Pd surface was readily reduced at our H_2O_2 reaction temperature of 313 K. This is evidenced by the rapidly decreasing difference in the H_2O_2 conversion values for the oxidized and reduced catalysts with time on stream in Figure 4b and the fact that 100% H_2O_2 conversion was observed for both catalysts at about the same time (Figure 4b and Table 1).

5. Conclusions

1. The blank experiment with the SiO_2 support demonstrated that the rate of H_2O_2 decomposition was negligible in the employed reactor system in the absence of Pd and, therefore, the measured H_2O_2 decomposition rates in the presence of the Pd/ SiO_2 catalysts were exclusively due to H_2O_2 reactions on Pd.

2. The rates of H_2O_2 decomposition were generally lower for the oxidized Pd/SiO₂ catalyst with a PdO surface than those for the reduced Pd/SiO₂ catalyst with a metallic surface (Figure 4, Table 1). The oxidized catalyst became reduced in the presence of gas-phase H_2 under the H_2O_2 reaction conditions, which was evidenced by its increased activity in H_2O_2 decomposition with time on stream (Figure 4b).

3. The mechanism of H_2O_2 decomposition can proceed through the O-O bond splitting and the O-H bond splitting reactions (Figure 5). The results of the DFT calculations on Pd surfaces (Figures 7 and 8) demonstrate that the O-H bond splitting reactions are endothermic, and they have higher activation energies (Table 2). In contrast, the O-O bond splitting reactions are exothermic, and they have lower activation energies (Table 2). However, in the absence of gas-phase H_2 , the energetically preferable O-O bond splitting reactions are not sufficient to produce molecular decomposition products. Therefore, the O-H bond splitting reactions are required, and they become rate determining. A combination of the O-O and O-H bond splitting reactions produces O_2 and H_2O .

4. The rates of H_2O_2 decomposition in the presence of gas-phase H_2 were higher than those under N_2 , which acted as an inert (Figure 3, Table 1). The results of the DFT calculations demonstrate that this activity increase is caused by a change in the reaction mechanism of H_2O_2 decomposition. The energetically preferable O-O bond splitting reactions (Table 2) become sufficient in the decomposition of H_2O_2 because the formed OH groups can readily react with adsorbed H species from gas-phase H_2 and produce H_2O as the decomposition product. The O-H bond splitting reactions with high activation energies are no longer required in this case.

5. The rate of H_2O_2 decomposition in the presence of gas-phase propylene was lower than that under N_2 for the reduced (metallic) Pd/SiO₂ catalyst (Figure 3a, Table 1) due to blocking of Pd active sites by the hydrocarbon species formed on the surface by propylene (Figure 2).

Although propylene does not directly participate in H_2O_2 decomposition reactions, both the propylidyne species formed in the dissociative propylene adsorption (Figure 2b, Reaction 3) and the molecularly adsorbed di- σ -bonded propylene species (Figure 2a, Reaction 2) are more strongly bound (more stable) than the H_2O_2 adsorbed species (Figure 5a, Reaction 4). Therefore, the hydrocarbon species compete with H_2O_2 for adsorption sites and act as surface spectator species.

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Table 1. H₂O₂ conversion over the reduced (metallic) and oxidized Pd/SiO₂ catalysts after 60 min of time on stream or time on stream to 100% conversion, if earlier, in the presence of gas-phase N₂, H₂ and C₃H₆.

Catalyst / H ₂ O ₂ Conversion, %	N ₂	H ₂	C ₃ H ₆
Reduced Pd	91	33 min	68
Oxidized Pd	31	33 min	33

Table 2. Reaction energies (and activation energies – numbers in brackets), kJ/mol, obtained with DFT calculations on the Pd(111) surfaces: (1) clean (Figure 7), (2) with pre-adsorbed H₂ (Figure 8a), (3) with pre-adsorbed C₃H₆ as propylidyne and atomic hydrogen species (Figure 8b) and (4) as di-σ-bonded C₃H₆ species (Figure 8c).

Reaction / Surface	Pd(111)	Pd(111) + 2H*	Pd(111) + C ₃ H ₅ * + H*	Pd(111) + C ₃ H ₆ *
H ₂ O ₂ + * = H ₂ O ₂ *	-55	-55	-41	-55
H ₂ O ₂ * + * = 2OH*	-196 (10)	-169 (10)	-164 (15)	-188 (12)
H ₂ O ₂ * + * = OOH* + H*	8 (70)	22 (75)	41 (88)	16 (75)
OOH* + * = OO* + H*	12	24	27	12

Figure captions

Figure 1. Pd particle size histograms and representative TEM images for the (a) reduced and (b) oxidized 2 wt % Pd/SiO₂ catalysts.

Preferred size: Single column with a width of 90 mm

Figure 2. Structures obtained with DFT calculations for (a) molecularly adsorbed propylene on Pd as di- σ -bonded C₃H₆* species and (b) dissociatively adsorbed propylene on Pd as propylidyne C-CH₂-CH₃* and H* species. The full 3×3×5 Pd periodic unit cell is shown for each structure. This unit cell was used to construct an infinite Pd(111) surface.

Single column: width 70 mm

Figure 3. Decomposition of H₂O₂ in a methanol solution in the presence of gas-phase N₂, H₂ and C₃H₆ at 313 K in a batch reactor as a function of time on stream for (a) the reduced Pd/SiO₂ catalyst with a metallic Pd surface and (b) the oxidized Pd/SiO₂ catalyst with a PdO surface.

1.5 column: width 140 mm

Figure 4. Decomposition of H₂O₂ in a methanol solution at 313 K in a batch reactor as a function of time on stream for the reduced and oxidized Pd/SiO₂ catalysts in the presence of gas-phase (a) N₂, which acted as an inert, (b) H₂ and (c) C₃H₆.

Double column: width 165 mm

Figure 5. Reaction steps in H₂O₂ decomposition on Pd evaluated with DFT calculations: (a) adsorption, $\text{H}_2\text{O}_2 + * = \text{H}_2\text{O}_2^*$, (b) O-O bond splitting, $\text{H}_2\text{O}_2^* + * = 2\text{OH}^*$, (c) first O-H bond splitting, $\text{H}_2\text{O}_2^* + * = \text{OOH}^* + \text{H}^*$, (d) second O-H bond splitting, $\text{OOH}^* + \text{H}^* + * = \text{OO}^* + 2\text{H}^*$. The calculated activation and reaction energies are summarized in Table 2.

1.5 column: width 130 mm

Figure 6. Reaction pathways with transition states in H₂O₂ decomposition on a clean Pd(111) surface: (a) O-O bond splitting reaction with the formation of two OH surface species and (b) O-H bond splitting reaction with the formation of OOH and H surface species. Top view. The top number for each configuration shows the energy in kJ/mol relative to the adsorbed H₂O₂, and the lower number shows either the O-O distance in nm for the O-O bond splitting or the O-H distance in nm for the O-H bond splitting.

Double column: width 170 mm

Figure 7. Structures in H₂O₂ decomposition reactions on a clean Pd(111) surface: (a) H₂O₂^{*}, (b) 2OH^{*}, (c) OOH^{*} + H^{*}, (d) OO^{*} + 2H^{*}. Top view. Only two top Pd layers are shown for clarity.

1.5 column: width 140 mm

Figure 8. Structures of adsorbed H₂O₂ on additional Pd(111) surfaces used in the evaluation of H₂O₂ decomposition reactions: (a) with pre-adsorbed hydrogen as 2H^{*}, (b) with pre-adsorbed propylene as propylidyne C-CH₂-CH₃^{*} and H^{*}, (c) with pre-adsorbed propylene as di-σ-bonded C₃H₆^{*}. Top view. Only two top Pd layers are shown for clarity.

1.5 column: width 135 mm

Figures

Figure 1. Pd particle size histograms and representative TEM images for the (a) reduced and (b) oxidized 2 wt % Pd/SiO₂ catalysts.

Single column: width 90 mm

Figure 2. Structures obtained with DFT calculations for (a) molecularly adsorbed propylene on Pd as di- σ -bonded C_3H_6^* species and (b) dissociatively adsorbed propylene on Pd as propylidyne $\text{C-CH}_2\text{-CH}_3^*$ and H^* species. The full $3\times 3\times 5$ Pd periodic unit cell is shown for each structure. This unit cell was used to construct an infinite Pd(111) surface.

Single column: width 70 mm

Figure 3. Decomposition of H_2O_2 in a methanol solution in the presence of gas-phase N_2 , H_2 and C_3H_6 at 313 K in a batch reactor as a function of time on stream for (a) the reduced Pd/SiO_2 catalyst with a metallic Pd surface and (b) the oxidized Pd/SiO_2 catalyst with a PdO surface.

1.5 column: width 140 mm

Figure 4. Decomposition of H_2O_2 in a methanol solution at 313 K in a batch reactor as a function of time on stream for the reduced and oxidized Pd/SiO_2 catalysts in the presence of gas-phase (a) N_2 , which acted as an inert, (b) H_2 and (c) C_3H_6 .

Double column: width 165 mm

Figure 5. Reaction steps in H_2O_2 decomposition on Pd evaluated with DFT calculations: (a) adsorption, $\text{H}_2\text{O}_2 + * = \text{H}_2\text{O}_2^*$, (b) O-O bond splitting, $\text{H}_2\text{O}_2^* + * = 2\text{OH}^*$, (c) first O-H bond splitting, $\text{H}_2\text{O}_2^* + * = \text{OOH}^* + \text{H}^*$, (d) second O-H bond splitting, $\text{OOH}^* + \text{H}^* + * = \text{O}_2^* + 2\text{H}^*$. The calculated activation and reaction energies are summarized in Table 2.

1.5 column: width 130 mm

Figure 6. Reaction pathways with transition states in H_2O_2 decomposition on a clean Pd(111) surface: (a) O-O bond splitting reaction with the formation of two OH surface species and (b) O-H bond splitting reaction with the formation of OOH and H surface species. Top view. The top number for each configuration shows the energy in kJ/mol relative to the adsorbed H_2O_2 , and the lower number shows either the O-O distance in nm for the O-O bond splitting or the O-H distance in nm for the O-H bond splitting.

Double column: width 170 mm

Figure 7. Structures in H₂O₂ decomposition reactions on a clean Pd(111) surface: (a) H₂O₂*, (b) 2OH*, (c) OOH* + H*, (d) OO* + 2H*. Top view. Only two top Pd layers are shown for clarity.

1.5 column: width 140 mm

Figure 8. Structures of adsorbed H_2O_2 on additional Pd(111) surfaces used in the evaluation of H_2O_2 decomposition reactions: (a) with pre-adsorbed hydrogen as 2H^* , (b) with pre-adsorbed propylene as propylidyne $\text{C-CH}_2\text{-CH}_3^*$ and H^* , (c) with pre-adsorbed propylene as di- σ -bonded C_3H_6^* . Top view. Only two top Pd layers are shown for clarity.

1.5 column: width 135 mm

Graphical Abstract: 5 x 11 cm