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A study of the apparent desorption energy for OH in the water formation reaction on a palladium catalyst

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In the H_2/O_2 reaction, the desorption of OH from a polycrystalline palladium foil has been studied with Laser-Induced Fluorescence (LIF) as a function of the hydrogen mixing ratio, α_{H_2}, and the temperature. The water production as a function of α_{H_2} was also monitored with microcalorimetry. The apparent desorption energy, E^a_{OH}, for OH has been measured from $\alpha_{H_2} = 0\%$ to $\alpha_{H_2} = 74\%$. At $\alpha_{H_2} = 0\%$, E^a_{OH} was measured to be 143 ± 7 kJ/mol; the apparent desorption energy then increases linearly with α_{H_2} to a maximum value of 223 ± 6 kJ/mol at $\alpha_{H_2} = 40\%$. At higher α_{H_2}, the apparent desorption energy was measured to be constant at about 200 kJ/mol. The maximum in apparent desorption energy at $\alpha_{H_2} = 40\%$ occurs at the same α_{H_2} as the maximum in water production. This phenomenon has also been reported for the platinum metal, although at an α_{H_2} value of 20%. The relative coverage of intermediates and products on the palladium catalysts was obtained using Chemkin.

KEY WORDS: catalysis; palladium; polycrystalline surface; water formation reaction; OH hydroxyl; apparent desorption energy; laser-induced fluorescence; high temperature kinetics.

1. Introduction

It is relevant to study OH desorption because the OH molecule is an important intermediate in catalytic combustion of hydrocarbons [1] and it is also central to the water formation reaction (the H_2/O_2 reaction); see for example [2–6]. The OH molecules in the gas phase are conveniently probed with laser spectroscopy because of their rather short lifetime and reactive nature. To obtain the OH molecules in the gas phase, to be detectable with, for example, Laser-Induced Fluorescence (LIF), information about desorption energies and coverage is of importance. The first OH molecule outside a platinum catalyst was detected in the late 1970s with LIF by the group of Lin [7]. Soon afterward, OH was detected on a Pt(111) surface by Fisher *et al.* [8] using a combination of ultraviolet photoemission spectroscopy (UPS), X-ray photoemission spectroscopy (XPS) and electron energy-loss spectroscopy (EELS). The OH molecule and the water formation reaction have since been studied with laser spectroscopy as well as surface-sensitive techniques and mass spectrometry; see for example [4,9–18].

Although the water formation reaction on primarily platinum catalysts has been given much attention throughout the years, there are still uncertainties and more work has to be done. Mechanisms for the water formation reaction have been suggested for both palladium and platinum; see for example [15] and references therein. The most important reactions for combustion of hydrogen on a palladium or platinum catalyst are summarized in table 1. In [15], we presented a new mechanism for water formation on palladium derived with Chemkin on the basis of experimental data, which in addition was compared with previous simulations and measurements for platinum. The palladium metal in comparison to platinum is more prone to form stable hydrides and oxides. In [15], we presented a thorough literature study on the subject. However, at the high temperatures and moderate pressures we will use in this study, the oxide and hydride formation is not believed to influence the catalytic properties of the palladium metal. Moreover, in [15], the yield of OH and the water production were investigated as a function of the hydrogen mixing ratio, α_{H_2}, which is defined as

$$\alpha_{H_2} = \frac{p_{H_2}}{p_{H_2} + p_{O_2}}. \qquad (1)$$

The maximum in water production occurs at different α_{H_2} for platinum and palladium, but the maximum in OH desorption was seen at about the same α_{H_2} for the two metals. The apparent desorption energy for OH was also measured for two different α_{H_2}. It was also noticed that the OH desorption was found to have a first-order coverage dependence; the initial sticking coefficients of hydrogen and oxygen were estimated to be about a factor of 10 larger on palladium than on platinum, and the decomposition of water had a more significant influence upon the OH formation on palladium than on platinum. This study will present a further analysis on the OH desorption process from a palladium catalyst.

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Table 1

A general mechanism for water formation on a catalytic surface. The *-symbol denotes that the atom or molecule requires one surface site

Adsorption and desorption of reactants	
S1	$H_2 \rightarrow 2H^*$
S2	$2H^* \rightarrow H_2$
S3	$O_2 \rightarrow 2O^*$
S4	$2O^* \rightarrow O_2$
Langmuir–Hinshelwood surface reactions	
S5	$H^*+O^* \iff OH^*$
S6	$H^*+OH^* \iff H_2O^*$
S7	$OH^*+OH^* \iff H_2O^*+O^*$
Desorption and adsorption of products and intermediate species	
S8	$H_2O \rightarrow H_2O^*$
S9	$H_2O^* \rightarrow H_2O$
S10	$OH \rightarrow OH^*$
S11	$OH^* \rightarrow OH$
S12	$O \rightarrow O^*$
S13	$O^* \rightarrow O$
S14	$H \rightarrow H^*$
S15	$H^* \rightarrow H$

There are, as far as we are concerned, only three previous studies on the OH apparent desorption energy for palladium [15,20,21], a few more for platinum [21–26], and two for rhodium [21,27] and nickel respectively [21,28]; Ljungström *et al.* [21] also studied the OH apparent desorption energy for iridium. An overview of the results is shown in table 2. In [23,26], apparent desorption energies were measured on both a polycrystalline and a single-crystal platinum catalyst. Even when applying the same experimental conditions, different apparent desorption energies for the two types of catalysts were measured.

In this work we have studied the apparent desorption energy of OH from a polycrystalline palladium catalyst with LIF in the whole α_{H_2} range. We have also, for all α_{H_2}, obtained the relative coverage of intermediates and products theoretically with Chemkin; for a recent theoretical analysis of platinum, see [19]. Our results on palladium will also be discussed and compared to apparent desorption measurements on platinum and also rhodium, nickel and iridium. Furthermore, we will also discuss the water formation in context to the apparent desorption energy.

There are several important aspects to the study of the OH radical within the water formation reaction on noble metal catalysts. Foremost, the availability of high temperature kinetic data on, for example, the palladium catalyst is limited, and also the importance of the different routes for water formation is debated. Studies of the OH desorption, especially in comparison of other catalysts, can give important information in perspective of catalytic combustion. Generally, knowledge about coverage and activation energies for OH desorption is a fundamental part of the understanding of the overall

Table 2

A summary of OH apparent desorption energy measurements for various catalysts

Metal	Type of catalyst	α_{H_2} (%)	E_{OH}[a] (kJ/mol)	Reference
Palladium	Polycrystalline wire	4–20	200, $T < 1210$ K	[20]
Palladium	Polycrystalline wire	4–20	84, $T > 1210$ K	[20]
Palladium	Polycrystalline foil	17	200	[15]
Palladium	Polycrystalline foil	20	138	[21]
Palladium	Polycrystalline foil	45	220	[15]
Palladium	Polycrystalline wire	62.5	251	[20]
Platinum	Single crystal Pt(111)	Close to 0	135	[26]
Platinum	Single crystal Pt(111)	17	109	[23]
Platinum	Single crystal Pt(111)	>20	193	[26]
Platinum	Single crystal Pt(111)	50	124	[23]
Platinum	Single crystal Pt(111)	80	145	[23]
Platinum	Polycrystalline foil	0	140	[25]
Platinum	Polycrystalline foil	1	160	[24]
Platinum	Polycrystalline foil	5	172	[21]
Platinum	Polycrystalline foil	9	134	[23]
Platinum	Polycrystalline foil	20	217	[25]
Platinum	Polycrystalline foil	91	176	[23]
Rhodium	Polycrystalline foil	2	113	[27]
Rhodium	Polycrystalline foil	5	175	[27]
Rhodium	Polycrystalline foil	13	105	[21]
Nickel	Polycrystalline wire	0.5	117	[28]
Nickel	Polycrystalline foil	31	Not able to measure	[21]
Nickel	Polycrystalline wire	33	163	[28]
Nickel	Polycrystalline wire	99.7	159	[28]
Iridium	Polycrystalline foil	5	121	[21]

kinetics of the water formation on, for example, a palladium catalyst.

2. Theory

Adsorption of atoms and molecules onto a metal surface does not usually require any activation energy. However, desorption of atoms and molecules is generally an activated process and a certain desorption energy is needed for the desorption to take place. The OH molecule requires a catalyst temperature above 900 K to desorb in measurable quantities for detection with LIF [25]. The desorbed OH flux, I_{OH}, can in its simplest form be written as

$$I_{\mathrm{OH}} = \theta_{\mathrm{OH}}(T) A_{\mathrm{OH}} \exp\left(-\frac{E^d_{\mathrm{OH}}}{k_{\mathrm{B}} T}\right), \tag{2}$$

where $\theta_{\mathrm{OH}}(T)$ is the temperature-dependent coverage, A_{OH} the preexponential, E^d_{OH} the desorption energy, k_{B} the Boltzmann constant and T the temperature. As the LIF experiments do not provide us with much information about the temperature-dependent coverage, $\theta_{\mathrm{OH}}(T)$, the desorption energy is not straightforward to measure. However, the apparent desorption energy, E^a_{OH}, can be measured with LIF. The apparent desorption energy contains the T-dependence of $\theta_{\mathrm{OH}}(T)$ and is defined as

$$E^a_{\mathrm{OH}} = -k_{\mathrm{B}} \frac{\partial}{\partial(1/T)} \ln(I_{\mathrm{OH}}). \tag{3}$$

The value of E^a_{OH} is obtained from the slope of a traditional Arrhenius plot ($\ln(I_{\mathrm{OH}})$ vs $1/T$).

In order to theoretically reproduce the maxima of OH and H_2O as a function of α_{H_2}, the OH desorption energy, E^d_{OH}, was found necessary to have a first-order coverage dependence [15]:

$$E^d_{\mathrm{OH}}(\theta) = E^d_{\mathrm{OH}}(0) - B\theta \tag{4}$$

where $E^d_{\mathrm{OH}}(\theta)$ is the desorption energy at coverage θ; $E^d_{\mathrm{OH}}(0)$ is the desorption energy at zero coverage, discussed as E^d_{OH} above; B is a constant equal to 100 kJ/mol according to [15]; and θ is the total coverage of products and intermediates, ranging from zero for an empty surface to one for a fully covered surface. The desorption energy is a measure of the Pd–OH bond. However, it is important to remember that variation of the apparent desorption energy with varying α_{H_2} is a kinetic effect and not primarily due to changes in the Pd–OH bond energy.

3. Experimental

The experimental set-up has previously been extensively described; see for example [4,12,29]. Briefly, it consists of a Roots-pumped (Balzers WKP 250 A) stainless-steel chamber. The catalyst was a resistively heated polycrystalline palladium foil (Goodfellow 99.99 + %) with the dimensions $3.8 \cdot 20 \cdot 0.025$ mm. Frequency-doubled light from an excimer-pumped dye laser (Lambda Physik EMG 102 E and FL 2002 E) was used to excite the OH molecules. The light from the dye laser was tunable and was scanned, around $\lambda = 307$ nm, over the $X^2\Pi(v'' = 0) \leftarrow A^2\Sigma^+(v' = 0)$ band in the OH molecule. The $R_1(5)$ transition was used for the measurements. The OH fluorescence was monitored in two dimensions with an ICCD camera (Princeton Instruments) perpendicular to the laser sheet. The flow of the hydrogen and oxygen gases was regulated with two mass flow controllers (Vacuum General FC6-21). The total gas flow was set to 100 SCCM. The gas composition at the inlet was calibrated with a quadrupole mass spectrometer (Balzers QMG 420). The total gas pressure in the chamber was 13 Pa and was measured with a capacitance manometer (MKS 227AAG). The temperature of the catalyst was varied between 1050 K and 1400 K, and kept constant with a Labview-based controller. The value of the desorbed flux of OH, I_{OH}, at each temperature was obtained from a Matlab program by integrating the OH fluorescence intensity for each image from 0.2 to 6 mm outside the catalytic foil. The water production was measured in the same experimental set-up with microcalorimetry.

4. Results and discussion

In this study, the apparent desorption energy for OH on a polycrystalline palladium foil has been measured from $\alpha_{\mathrm{H}_2} = 0\%$ to $\alpha_{\mathrm{H}_2} = 74\%$ in order to increase the understanding of the OH desorption process. In addition, for palladium there are no previous complete measurements of the E^a_{OH} in the whole α_{H_2}-range. In this work, the total pressure was 13 Pa and the gas flow was set to 100 SCCM. The result is shown in figure 1. The apparent desorption energy for each α_{H_2} was derived from a traditional Arrhenius plot. For each Arrhenius plot, the uncertainty was calculated from a least-square fit of a straight line to the experimental data. Several measurements were done for each α_{H_2} to obtain the values presented in figure 1. Moreover, it is seen in figure 1 that the apparent desorption energy is increasing from, on average, 143 ± 7 kJ/mol at $\alpha_{\mathrm{H}_2} = 0\%$ to about 223 ± 6 kJ/mol at $\alpha_{\mathrm{H}_2} = 40\%$. However, at $\alpha_{\mathrm{H}_2} = 50\%$ and onward, the apparent desorption energy seems to be rather constant around 200 kJ/mol, but at a lower value than for $\alpha_{\mathrm{H}_2} = 40\%$. At $\alpha_{\mathrm{H}_2} = 74\%$ the E^a_{OH} value seems to be somewhat lower than for the other measured E^a_{OH} values above $\alpha_{\mathrm{H}_2} = 40\%$. However, at $\alpha_{\mathrm{H}_2} = 74\%$ the yield of OH is very low (see figure 2) and therefore difficult to measure accurately, which can explain the observed discrepancy. In addition

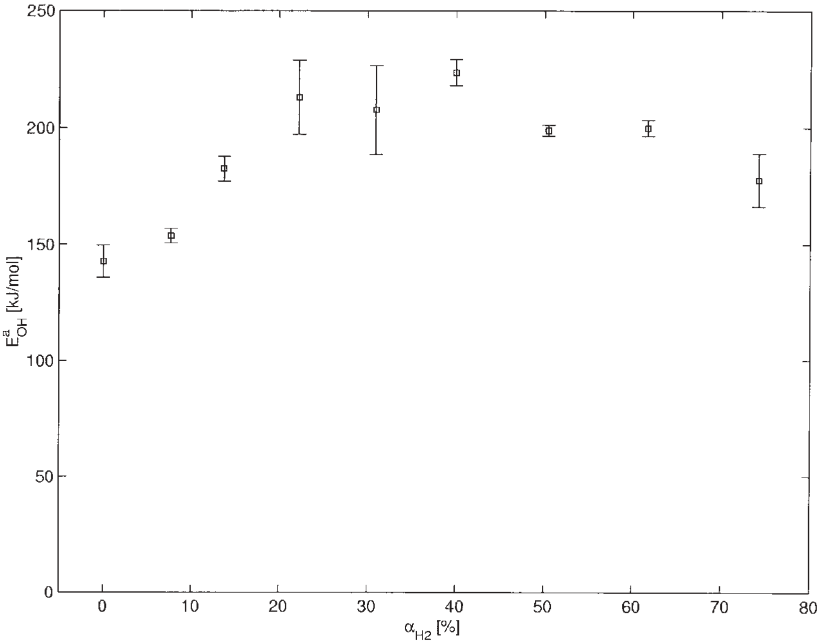

Figure 1. The apparent desorption energy for OH on palladium measured as a function of the hydrogen mixing ratio, α_{H_2}. The total pressure was 13 Pa and the flow was set to 100 SCCM. For each α_{H_2}, three measurements were done. The experimental data for each α_{H_2} were combined into one Arrhenius plot to obtain the results shown here.

to the experimental results, the relative coverage of products and intermediates as a function of α_{H_2} was obtained using Chemkin; for details of the simulations and the model used, see [15]. The relative coverage was calculated for a temperature of 1300 K, a flow of 100 SCCM and a pressure of 13 Pa. The result is shown in figure 3.

The water production and OH desorption were also measured as a function of α_{H_2} at the same experimental conditions as described above; see figure 2. Both the OH desorption and water production increase with α_{H_2} to a maximum, but at different α_{H_2} values. The maximum in OH desorption ($\alpha_{H_2,OH_{max}}$) occurs at $\alpha_{H_2,OH_{max}} = 10\%$ and the maximum in water production ($\alpha_{H_2,H_2O_{max}}$) is at about $\alpha_{H_2,H_2O_{max}} = 40$–$45\%$. It is interesting to note that the change in apparent desorption energy occurs at the same α_{H_2} as the maximum in water production. The same phenomenon has also previously been noticed on

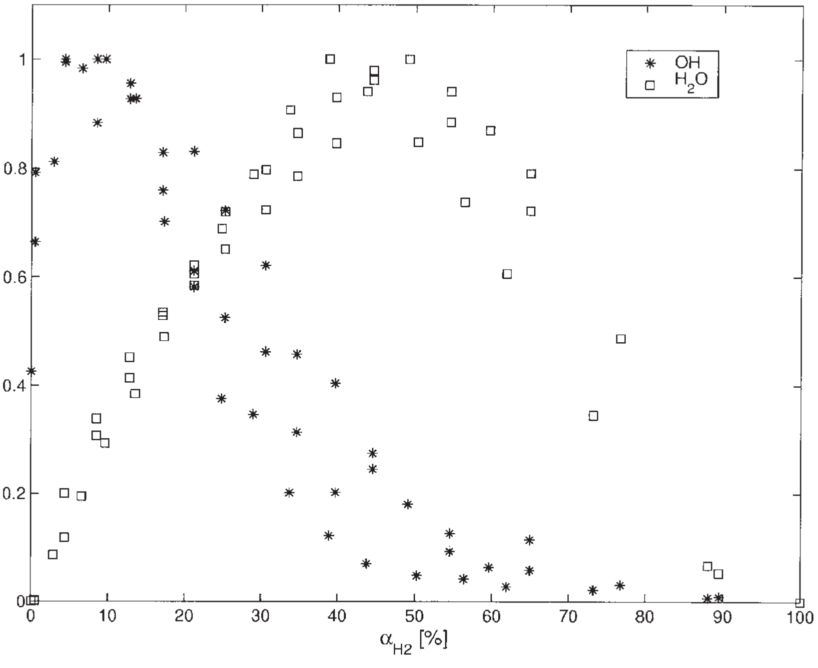

Figure 2. The yield of OH and the water production as a function of α_{H_2}. The temperature of the catalyst was 1300 K, the total pressure was 13 Pa and the flow was set to 100 SCCM. The curves are normalized to unity independently of each other.

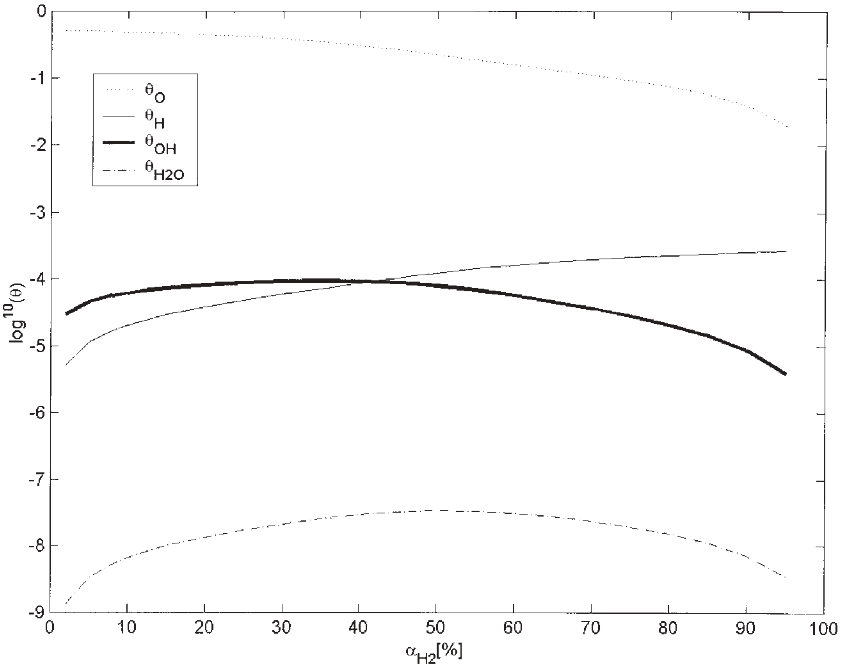

Figure 3. The relative coverage of products and intermediates as a function of α_{H_2}, derived theoretically with Chemkin. The temperature of the catalyst was 1300 K, the pressure 13 Pa and the flow was set to 100 SCCM.

platinum. However, the maximum in water production occurs at $\alpha_{H_2,H_2O_{max}} = 20\%$ for platinum and the change in apparent desorption energy also happens at $\alpha_{H_2} = 20\%$; see for example [11,25,26]. Moreover, in figure 3, it is interesting to note that at $\alpha_{H_2,H_2O_{max}}$ the relative coverage of hydrogen is becoming larger than the relative coverage of OH.

4.1. Variations in E^a_{OH} with α_{H_2}

The production of OH is believed to be the rate-limiting step for water formation (reaction S5 in table 1); see for example [30]. The OH molecule can be formed from three different paths, reaction S5 and the reverse of S6 and S7; see table 1. The formation of OH is highly dependent on the coverage of reactants on the surface. For low coverage, oxygen is believed to be the dominant species on the catalytic surface. When α_{H_2} is increasing, i.e. more hydrogen is added, all hydrogen reacts further to form water. At the maximum in water production, the total surface coverage is supposed to be low. If we assume that the maximum in water production $\alpha_{H_2,H_2O_{max}}$ occurs when the transport of reactants to the surface is stoichiometric, the ratio of the initial sticking coefficients for hydrogen and oxygen can be derived from the position of the $\alpha_{H_2,H_2O_{max}}$; see [4,16] for a more detailed description. The initial sticking coefficient of hydrogen, $S_{H_2}(0)$, and that of oxygen, $S_{O_2}(0)$, seem to differ significantly for palladium and platinum. For example, $S_{H_2}(0)$ and $S_{O_2}(0)$ for platinum have been reported to be 0.046 and 0.023 respectively [4]. Values for $S_{H_2}(0)$ and $S_{O_2}(0)$ on palladium were derived from a theoretical model based on experimental data [15] to be $S_{H_2}(0) = 0.32$ and $S_{O_2}(0) = 0.45$. Because of the higher initial sticking coefficients, the surface coverage of reactants is generally believed to be higher on palladium than for platinum, especially the coverage of oxygen. The relative coverage of products and intermediates on a palladium surface is shown in figure 3. A similar plot for a platinum surface can, for example, be found in [26]; comparing that graph with figure 3, differences in coverage on palladium and platinum are clearly seen. The diversity in initial sticking coefficients and coverage is a possible explanation for the different positions of $\alpha_{H_2,H_2O_{max}}$ and also the switch in apparent desorption energies for platinum and palladium at different α_{H_2}.

In figure 1 it is seen that the apparent desorption energy increases linearly with α_{H_2}. Fujimoto *et al.* [31] attributed such behavior to a situation where some surface sites bind more strongly to the OH molecule than other. At low α_{H_2}, the surface is oxygen-rich; the desorption of OH then primarily occurs from the weaker surface sites, which corresponds to a lower apparent desorption energy. When α_{H_2} is increasing, water is formed from OH at the weaker sites, leaving the OH molecules at the stronger sites, resulting in a higher apparent desorption energy at higher α_{H_2}. Williams *et al.* [24] explained the variation of E^a_{OH} by the hydrogen coverage, which was believed to increase with decreasing temperature. Fridell *et al.* [26] also explained the variation in E^a_{OH} for a platinum catalyst with variations in the coverage. At low α_{H_2}, a rapid increase in temperature would lead to an excess of oxygen on the surface because the desorption energy for O_2 is much larger than it is for H_2 (see, for example, [15]), which would result in a low coverage of OH giving low apparent desorption energies. At higher α_{H_2}, there is also a similar decrease in the hydrogen coverage with increasing temperature, but not as pronounced as the decrease of the oxygen coverage at the lower α_{H_2}. This would give larger E^a_{OH} at higher α_{H_2} and temperature. The trend in increasing E^a_{OH} with α_{H_2} is similar for both palladium and platinum. The increase in E^a_{OH} for palladium can also most probably be explained by the changes in coverage, as discussed above in [26] and [24]. However, the maximum in E^a_{OH} and water production occurs at different α_{H_2} for platinum and palladium, which is believed to be a result of the different values of the initial sticking coefficients, i.e. the coverage on palladium and platinum.

In addition, for palladium, the value of the apparent desorption energy seems to be highest at $\alpha_{H_2,H_2O_{max}}$ and then it decreases somewhat for higher α_{H_2}; this behavior is not seen in the platinum case. Furthermore, it is important to remember that the OH desorption energy is found to be coverage-dependent for palladium [15], which is also a difference compared to platinum.

4.2. *Previous studies of E^a_{OH}*

The OH apparent desorption energy has been measured earlier on several catalysts. A summary is presented in table 2.

4.2.1. *Palladium*

There are three different studies for palladium [15,20,21]. In [20], the apparent desorption energy for OH has been measured outside a coiled polycrystalline palladium wire with LIF. The total pressure in the chamber varied between 7 and 9 Pa. At $\alpha_{H_2} = 62.5\%$, the apparent desorption energy was measured to be 251 kJ/mol. For $4\% \alpha_{H_2} < 20\%$, two different apparent desorption energies were observed, because the Arrhenius plot showed a nonlinear behavior. For temperatures lower than 1210 K, the apparent desorption energy was measured to be 200 kJ/mol and for temperatures higher than 1210 K, within the same Arrhenius plot, E^a_{OH} was determined to be 84 kJ/mol. In [21], E^a_{OH} was measured with LIF to be 138 kJ/mol on a polycrystalline palladium foil at $\alpha_{H_2} = 20\%$ and a total pressure of 13 Pa. In [15], E^a_{OH} was determined with LIF to be 200 kJ/mol at $\alpha_{H_2} = 17\%$, and 220 kJ/mol at $\alpha_{H_2} = 45\%$; the total pressure was 13 Pa.

4.2.2. *Platinum*

Platinum is the most studied system for OH apparent desorption energies; see for example [21–26]. In the study by Hsu *et al.* [23], the OH apparent desorption energy was measured with LIF, and compared on both a Pt(111) and a polycrystalline platinum catalyst. On the Pt(111) surface, E^a_{OH} was measured to be 109 kJ/mol at $\alpha_{H_2} = 17\%$, 124 kJ/mol at $\alpha_{H_2} = 50\%$, and 145 kJ/mol at $\alpha_{H_2} = 80\%$. For the polycrystalline foil, E^a_{OH} was measured to be 134 kJ/mol at $\alpha_{H_2} = 9\%$, and 176 kJ/mol at $\alpha_{H_2} = 91\%$. It was concluded that the nonlinearity of the Arrhenius plots was more prominent in the single-crystal case. The curvature at the high temperature end of the Arrhenius plot could be explained by a low coverage of hydrogen and oxygen. It was suggested that the irregularities on the polycrystalline surface enhanced the dissociative chemisorption of hydrogen and oxygen. This would maintain a high concentration of reactive species on the surface and keep the formation of OH as the rate-limiting step, resulting in a straight line in the Arrhenius plot. It was also seen that the apparent desorption energy was increasing with α_{H_2}. In [22], an extended study of [23], similar results were presented.

Apparent desorption energies were also measured with LIF and compared for a polycrystalline platinum foil and a Pt(111) surface in [26]. For both samples, the apparent desorption energy increases to a maximum at $\alpha_{H_2,H_2O_{max}}$ and then stays constant. However, E^a_{OH} values for the polycrystalline foil are significantly larger and have a larger spread. The apparent desorption energies for the Pt(111) surface also seemed to fit their model much better than those for the polycrystalline sample. For the Pt(111) surface, E^a_{OH} was measured to be 135 kJ/mol for α_{H_2} close to zero. At $\alpha_{H_2} > 20\%$, E^a_{OH} reaches a maximum value of about 193 kJ/mol. The values presented for the polycrystalline foil were originally from [25].

In the LIF study by Wahnström *et al.* [25], the apparent desorption energy on a polycrystalline platinum surface was seen to increase from 140 kJ/mol at $\alpha_{H_2} = 0\%$ to 217 kJ/mol at $\alpha_{H_2} = 20\%$; thereafter the value seems to be stable at 217 kJ/mol. The total pressure in the chamber was 13 Pa. By obtaining the temperature-dependent coverage from a kinetic model, the desorption energy, E^d_{OH}, was calculated to be 193 kJ/mol for $\alpha_{H_2} > 20\%$. In the comparative study by Ljungström *et al.* [21], the apparent desorption energy for OH on platinum was measured with LIF to be 172 kJ/mol at $\alpha_{H_2} = 5\%$. The OH apparent desorption energy from a polycrystalline platinum foil was also investigated with LIF by [24]. At $\alpha_{H_2} = 1\%$, a curvature in the Arrhenius plot was seen, and at the higher temperatures the apparent desorption energy was measured to be 160 kJ/mol.

4.2.3. *Rhodium*

Zum Mallen *et al.* [27] measured the apparent desorption energy with LIF for OH on a rhodium foil. At $\alpha_{H_2} = 2\%$, E^a_{OH} was determined to be 113 kJ/mol while at $\alpha_{H_2} = 5\%$ it was measured to be 175 kJ/mol. The total pressure was about 13 Pa. Moreover, Ljungström *et al.* [21] measured E^a_{OH} for OH on rhodium to be 105 kJ/mol for $\alpha_{\mathrm{H_2}} = 13\%$.

4.2.4. Nickel

Keiser *et al.* [28] studied the OH desorption with LIF from a polycrystalline nickel wire. Three values of the apparent desorption energy, E^a_{OH}, were reported: 117 kJ/mol at $\alpha_{\mathrm{H_2}} = 0.5\%$, 163 kJ/mol at $\alpha_{\mathrm{H_2}} = 33\%$, and 159 kJ/mol at $\alpha_{\mathrm{H_2}} = 99.7\%$. The total pressure was fixed at 263 Pa with argon as dilution gas and the desorbed OH molecules were detected with LIF. Moreover, at about $\alpha_{\mathrm{H_2}} = 20\%$, the apparent desorption energy seems to change from a higher value at high $\alpha_{\mathrm{H_2}}$ to a lower value at smaller $\alpha_{\mathrm{H_2}}$. Ljungström *et al.* [21] were not able to measure the OH apparent desorption energy for nickel.

4.2.5. Iridium

In the study by Ljungström *et al.* [21], the apparent desorption energy for OH from a polycrystalline iridium foil was measured to be 121 kJ/mol with LIF. No other studies for iridium were found.

4.3. Estimation of E^d_{OH}

A value of E^d_{OH} can be obtained from the desorbed flux of OH, I_{OH}, by using equation (2). In addition, the preexponential was set to $10^{13}\ \mathrm{s^{-1}}$ [15]; $\theta_{\mathrm{OH}}(T)$ was taken from figure 3, and the temperature was 1300 K. By using these data, the desorption energy, E^d_{OH}, can be calculated to be about 180 kJ/mol. Further, by use of equation (4) and the relative coverage from figure 3, it can be seen that $E^d_{\mathrm{OH}}(\theta)$ is increasing linearly with $\alpha_{\mathrm{H_2}}$. However, as we only have access to the relative coverage for the calculations, the value of E^d_{OH} presented here should merely be taken as guidance for further studies.

In summary, the values for E^a_{OH} presented in this study are in reasonable agreement with previous measurements; see figure 1 and table 2. Two values of E^a_{OH} were measured in our previous study [15] and those measurements seem to fit in well with the new complete study. The apparent desorption energy measured by Ljungström *et al.* [21] appears to be somewhat lower than our values. Their results were obtained with the same experimental chamber as ours, but their $\alpha_{\mathrm{H_2}}$ values were not calibrated with a mass spectrometer. After calibration, the true $\alpha_{\mathrm{H_2}}$ value seems to decrease, and bearing that in mind our values seem to be in better agreement. For lower $\alpha_{\mathrm{H_2}}$, our values appear to agree with the low temperature result of [20]. However, at high $\alpha_{\mathrm{H_2}}$, our values seem to be somewhat lower than the value reported in [20].

The results presented in this work are complementary experimental data that describe the behavior of the OH apparent desorption energy as a function of $\alpha_{\mathrm{H_2}}$. In addition, we present theoretical data for the relative coverage of intermediates and products on the palladium surface. Learning more about the coverage of reactants and intermediates on the palladium surface will be of importance in the future.

5. Conclusions

The temperature dependence of OH on a palladium surface has been studied as a function of $\alpha_{\mathrm{H_2}}$ in the temperature range 1050–1400 K. The apparent desorption energy, E^a_{OH}, was measured and it was clearly seen that E^a_{OH} increased linearly with $\alpha_{\mathrm{H_2}}$ to a maximum; then it decreased slightly and stayed constant. The apparent desorption energy differs from the desorption energy because it contains the temperature-dependent coverage. At $\alpha_{\mathrm{H_2}} = 0\%$, it was measured to be 142 ± 7 kJ/mol; the value increases with $\alpha_{\mathrm{H_2}}$ to a maximum at $\alpha_{\mathrm{H_2}} = 40\%$, which is $E^a_{\mathrm{OH}} = 223 \pm 6$ kJ/mol. Thereafter, at higher $\alpha_{\mathrm{H_2}}$, the apparent desorption energy seems to be constant at about 200 kJ/mol. Our measured values of E^a_{OH} are also in agreement with literature. The relative coverage of products and intermediates has been derived theoretically with Chemkin. The yield of OH and water production were also measured as a function of $\alpha_{\mathrm{H_2}}$ with LIF and microcalorimetry, respectively. For palladium, the maximum in apparent desorption energy occurs at the same $\alpha_{\mathrm{H_2}}$ value as the maximum in water production. This phenomenon is also noticed for platinum, but the maximum in water production on platinum appears at a different $\alpha_{\mathrm{H_2}}$ ($\alpha_{\mathrm{H_2}} = 20\%$) than for palladium.

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