Effect of oxygen on formic acid decomposition over Pd catalyst

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ABSTRACT

It is well known that Pd based catalyst deactivate during formic-acid decomposition in aqueous phase at mild temperatures. This study reports on a kinetic study of formic acid decomposition over Pd/γ-Al2O3 catalysts including the effect of traces of oxygen, as well as pretreatment of the catalysts and supported by in-situ Attenuated Total Reflection Infrared Spectroscopy experiments. The results show that deactivation of Pd/γ-Al2O3 catalysts can be suppressed by adding traces of oxygen. This is assigned to removal of adsorbed CO, poisoning the Pd surface, via oxidation to CO2. The activity of the catalyst during operation is maintained, promoting the H2 production compared to operation in absence of any oxygen. Clearly, oxygen oxidizes CO preferentially over H2 under the condition that the oxygen concentration is kept below 0.1 vol% in this study. Further increasing the oxygen concentration further increases conversion rate of formic-acid but also decreases the hydrogen yield significantly because formic acid oxidation and/or consecutive H2 oxidation become dominating. The results of this study are important because the effect of traces of oxygen from ambient has not been considered in most of the reports in literature. © 2020 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

In times of fossil fuel resources shortage and concern about CO2 emissions, the search for alternative and sustainable energy sources has become more pressing than ever. Hydrogen has attracted an increasing level of attention as an important energy vector and may play a significant role in power distribution in the future. However, due to the extremely low critical point and very low density of hydrogen gas, it is particularly difficult to store efficiently, especially on long term. Many molecules have been proposed as hydrogen carriers, e.g. ammonia [1], methanol [2], methane [3] as well as higher hydrocarbons [4]. Another option is formic-acid which can be produced from CO2 and green hydrogen [5–7], resulting in a carbon-neutral process. Hydrogenation of CO2 to formic acid requires either high pressure or operation below 0.1 vol% in this study. Further increasing the oxygen concentration further increases conversion rate of formic-acid but also decreases the hydrogen yield significantly because formic acid oxidation and/or consecutive H2 oxidation become dominating. The results of this study are important because the effect of traces of oxygen from ambient has not been considered in most of the reports in literature. © 2020 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

So far, all heterogeneous catalysts studies suffer from deactivation to some extent. However, the deactivation mechanism is still under debate. Ruthven et al. [24] proposed that deactivation is due to formation of palladium hydride, supposedly β-Pd hydride, which is suggested to be inactive. Hu et al. [25] suggested that catalyst deactivation is caused by occupation of active sites by protons, CO2, H2O and HCOO intermediate species. However, CO poisoning
is proposed most frequently to cause catalyst deactivation. CO adsorbs much more strongly on Pd than H₂ and CO₂, considering adsorption enthalpies of 150 kJ/mol for CO [27] at low coverage, versus 100 kJ/mol [28] and 80 kJ/mol [29] for H₂ and CO₂, respectively. Jiang et al. [18] confirmed presence of chemisorbed CO during formic-acid decomposition, using Attenuated Total Reflection Infrared Spectroscopy (ATR-IR).

CO adsorbed on Pd reacts easily with oxygen at room temperature forming CO₂, even in aqueous phase as e.g. observed with ATR-IR [30]. Therefore, it may be expected presence traces of oxygen could influence the formic acid decomposition reaction. It is remarkable that in several studies on formic acid decomposition in aqueous phase, the gas composition in the reactor is not clearly defined [18,20,23,31–35], while other studies were performed in a reactor open to ambient [14,36–40]. Only in a few studies oxygen was rigorously removed [24,41,42], but the influence of the oxygen concentration on formic-acid decomposition has not been reported yet. This study reports on the influence of the oxygen concentration on rate, selectivity and deactivation in formic-acid decomposition over Pd catalysts.

2. Experimental section

2.1. Materials

Commercial γ-Al₂O₃ powder purchased from BASF, characterized by a surface area of 195 m²/g, was used as catalyst supports in this study. Tetramminepalladium (II) nitrate solution (10 wt% in H₂O, 99.99%) was purchased in Sigma-Aldrich was used as catalyst precursor solution. Ammonium (50% v/v water), Formic-acid (≥98%) and sodium hydroxide were purchased from Sigma-Aldrich. Pre-mixed O₂ in Ar (0.1 vol%) and CO in Ar (10 vol%) was purchased from Linde. All the aqueous solutions were prepared using ultra pure water obtained with a water purification system (Millipore, Synergy).

2.2. Catalyst preparation

The Pd/γ-Al₂O₃ catalyst containing 1 wt% of palladium, was prepared by wet impregnating method. The method was described in elsewhere [43,44]. In brief, 10 g (0.098 mol) of the sieved support (size less than 20 μm) was calcined at 600 °C in air for 4 h to remove any organic pollutants. Then the support was suspended in 100 mL milliQ water, the pH of the solution was adjusted by adding 2 mL ammonium solution to maintain the pH around 9, checked with a pH meter in order to ensure electrostatic interaction of Pd (NH₄)₂[C₄H₆] with the negatively charged alumina surface. Then 3 g of the original palladium precursor solution (containing 1 mmol Pd (NO₃)₂·4NH₄) was added in the suspension slowly and stirred at room temperature for at least 1 h. Further, the solution was transferred to the rotary evaporator to remove the liquid during 2 h at 70 °C. Then the catalyst was calcined in air at 400 °C for 3 h (5 K/min), switched to N₂ gas for 20 min, followed by reduction in 50 vol% hydrogen diluted in nitrogen (total flow rate 60 mL/min) at the same temperature for 3 h. The catalysts were characterized and used in catalytic tests as prepared and without any further treatment.

2.3. Catalyst characterization

The BET surface area of the catalyst, degassed at 300 °C for 1 day, was determined with N₂-adsorption at 77 K (Micromeritics Tristar). The Pd loading on the alumina support was determined with X-ray fluorescence spectroscopy (XRF, Philips PW 1480). The metal surface area that is accessible was determined with CO chemisorption at room temperature (Chemisorb 2750, Micromeritics). Typically, the sample was reduced at room temperature in hydrogen for 1 h and flushed with He at the same temperature for 0.5 h. Then, CO was introduced as pulses and the response was recorded using a TCD detector. Pd particle sizes are estimated assuming hemispherical metal particles and assuming that the stoichiometric ratio of adsorbed CO and Pd surface atoms is one. X-ray photoelectron spectroscopy (XPS) was conducted on as-prepared catalysts by an Omicron Nanotechnology GmbH (Oxford Instruments) surface analysis system with a photon energy of 1486.7 eV (Al Kα X-ray source) with a scanning step size of 0.1 eV and a pass energy of 20 eV. Due to the poor electrical conductivity of sample surface, it is necessary to neutralize charge on the sample with an electron spray. The spectra were corrected using the binding energy of C 1s peak as a reference.

2.4. Catalytic tests

Activity and selectivity of the catalysts were measured in a 1 L batch reactor operated at 20 °C at atmospheric pressure. The glass reactor (DURAN® BAFFLED, WIDE MOUTH BOTTLE GLS 80®) has a diameter of 10.1 cm and height 22.2 cm. The reactor has four connections on the reactor lid for gas-in, gas-out, sampling and a stirring shaft equipped with 4 stirring blades.

The reaction condition is shown in Table 1. Typically, 0.1 g catalyst was suspended in 0.3 L milli-Q water and stirred at 625 rpm while flushing with a mixture gas of Ar and oxygen (between 0 and 2 vol% oxygen) with a flow rate of 50 mL/min for at least one hour to remove any gases dissolved in the water and gas in the 700 mL gas cap. The gas flow rates (NTP) were controlled using mass flow controllers (Brooks 5850S). The reaction was started by introducing 60 μL pure formic-acid solution. The initial pH was varied between 2 and 10 by adding the appropriate amount of sodium hydroxide (1 M solution) to the formic-acid solution. The stability experiments were performed by injecting additional 15 μL pure formic-acid, one hour after the first injection. This procedure was repeated three times.

The procedure described above includes experiments under Ar, in absence of any oxygen and this experiment is termed as inert-experiment. In addition, a semi-inert-experiment was conducted by flowing pure Ar (50 mL/min), like in the inert experiment, with the difference that the gas pipe inlet was positioned above the liquid level so that the dissolved oxygen as well as gasses produced during the experiment are very slowly removed from the water phase.

Additional experiments were performed after pretreatment with CO according the following procedure. The reactor was first flushed with inert for 90 min (99.9 vol% Ar, 60 mL/min), followed by reduction of the catalyst in 20 vol% H₂/Ar for 50 min (Flowrate 50 mL/min). After that, the reactor was again flushed with inert gas until no H₂ was detected in the outlet stream of the reactor. Then a gas mixture containing 10 vol% CO in Ar (Linde Gas Benelux B.V.),
50 mL/min) was fed to the reactor for 30 min, followed by flushing once more with inert gas for about 40 min (99.9 vol% Ar, 50 mL/min) to remove CO from the reactor. Finally, the experiment was initialized by adding formic-acid solution to the reactor while flowing with inert gas.

Samples were taken at different reaction times using a 2.5 mL syringe (BD Plastipak) and filtered through a syringe filter (PTFE, 0.2 μm, Whatman) in order to remove the catalyst. Formic-acid concentrations were measured with ion-chromatography (DIONEX, ICS 3000) equipped with an Ultimate autosampler. The gas products were measured with an online micro-GC, sampling every 5 min, measuring the concentrations of H₂, CO₂ and CO. The number of moles of H₂, CO₂ and CO were obtained by the integration over time of each of the observed flow rates, which were calculated using the concentration profile measured by GC and the total gas flow rate used in the experiment.

Formic-acid conversion and H₂, CO₂, CO yield were calculated according to equation (3), (4), (5) and (6), respectively.

\[
\text{HCOOH conversion} = \frac{n_{\text{HCOOH,0}} - n_{\text{HCOOH,t1}}}{n_{\text{HCOOH,0}}} \times 100
\]

\[
H_2 \text{ yield} = \frac{n_{\text{H}_2, t1}}{n_{\text{HCOOH,0}}} \times 100
\]

\[
CO_2 \text{ yield} = \frac{n_{\text{CO}_2, t1}}{n_{\text{HCOOH,0}}} \times 100
\]

\[
CO \text{ yield} = \frac{n_{\text{CO}, t1}}{n_{\text{HCOOH,0}}} \times 100
\]

\[n_{\text{HCOOH,0}}\text{ and } n_{\text{HCOOH,t1}}\text{ are the initial amount of formic-acid in moles and at t1, respectively. Likewise, } n_{\text{H}_2, t1}, n_{\text{CO}_2, t1}, \text{ and } n_{\text{CO}, t1}\text{ are the integral amounts of H}_2, \text{ CO}_2, \text{ and CO formed at t1 in moles, respectively.}
\]

The apparent turnover frequency (TOF) was calculated according equation (7), based on conversion at t1 lower than 20%.

\[
\text{TOF} = \frac{\text{conversion rate HCOOH}_{t1} \text{ mols} \times s^{-1}}{\text{mols of available surface Pd mols}}
\]

\[\text{The number of available Pd surface-atoms was obtained with CO-chemisorption.}\]

2.5. ATR-IR

The preparation of catalyst layer on the ATR crystal is described elsewhere [30,45–48]. Briefly, a suspension containing 0.1 g 1 wt% Pd/γ-Al₂O₃ dispersed in 20 mL 2-propanol was prepared. In order to prevent cracking of the catalyst layer, the suspension was sonicated with an ultrasonic processor (Fisher Scientific-705) for 1 h. Subsequently, the suspension was spray-coated on a trapezoidal ZnSe crystal (52.5 mm * 20 mm* 2 mm, facet angle 45°, Anadis instruments BV), which was placed on a hot plate at 150 °C, resulting in about 5 mg catalyst on the crystal. Then, the coated crystal was calcined at 300 °C (1 °C/min) for 1 h in N₂ atmosphere (20 mL/min). It was mounted in a home-build in-situ ATR-IR cell which has been described in detail elsewhere [45,46]. The cell was mounted in the sample compartment of an infrared spectrometer (Tensor 27, Bruker) equipped with a liquid nitrogen cooled MCT detector. All the liquid flows were pumped by a peristaltic pump (Verderflex) downstream of the ATR-IR cell to prevent formation of gas bubbles in the cell.

Once the cell was assembled in the IR spectrometer, it was flushed with Ar/H₂O with a flow rate of 0.5 mL/min until a stable water spectrum was obtained. Once the water spectrum was stable, the background spectrum was collected. Subsequently, the cell with the catalyst layer was flushed with formic-acid solution (10 mM) at pH 5 or pH 3, degassed with Ar before the experiment for at least 3 h. The catalysts in the ATR cell was exposed to the liquid flow during 10 min, where after the liquid flow was stopped, mimicking a batch reactor. ATR-IR spectra were recorded at room temperature (20 ± 1 °C) in an air-conditioned room. Each spectrum was acquired by averaging of 128 scans taken with a resolution of 4 cm⁻¹. The collected spectra were averaged over 60 s. The catalyst layers were reused a few time and comparable results were obtained, indicating that the catalyst layer is stable during the experiments.

3. Results

3.1. Catalyst characterization

Table 2 reports the properties of the Pd/γ-Al₂O₃ catalyst. The high surface area γ-Al₂O₃ support assisted to achieve high metal dispersion, as determined with CO-chemisorption. XPS measurements showed that the sample stored in ambient conditions contains 30% of the Pd in oxidized state (shown in Figure S1), in reasonable agreement with literature [19,39].

3.2. Formic-acid decomposition under inert atmosphere

Fig. 1 shows a typical result of a formic-acid decomposition experiment, showing the decreasing concentration of formic-acid as well as the concentrations of H₂ and CO₂ in the gas-stream during the experiment. CO was never detected in any experiment in this study. Note that the differences in the shape of the profiles are caused by the fact that the liquid phase can be considered as a batch reactor, the formic-acid concentration is converted with a decreasing rate in time. In contrast, the gas phase products are measured in the gas stream passing through the reactor and the low concentrations observed in the first half hour are due to the fact that the concentrations of H₂ and CO₂ in the gas cap have to build up first. Consequently, information on gas-phase products is delayed. Nevertheless, the amount of H₂ and CO₂ produced and removed from the reactor at a certain time can be calculated by the integration over time of the flow rate of each product, which is based on its concentration profile and the Ar flow rate, as is shown in Fig. 2a.

Fig. 2a shows the amount of formic-acid converted (based on the formic-acid concentration in Fig. 1) and the amounts of H₂ and CO₂ produced (calculated as explained above). Fig. 2b shows in more detail the same for the initial phase of the experiment. The results clearly show that the reaction rate is constant during the first half our, whereas the amounts of gas-phase products show a clear delay, as discussed above. Therefore, the initial turnover frequencies are calculated based on conversion of formic-acid at low conversion. Furthermore, the reaction becomes extremely slow after typically one hour, as can be seen in Fig. 2a where both profiles for the consumption of formic-acid and the cumulative amount of gas-phase products are flattened. Additionally, H₂ and CO₂ are produced in equal amount, in agreement with the stoichiometry of the decomposition reaction. Also, the number of

| Catalyst | Pd/γ-Al₂O₃ |
|----------|------------|
| Catalyst specific surface area, m²/g | 195 |
| Metal loading, wt% | 0.9 |
| CO uptake, μmol/g | 31.3 |
| Metal dispersion, % | 38 |
| Mean metal particle size, nm | 2.8 |
| Pd⁰/Pd²⁺ | 2.3 |
moles formic-acid (0.5 mmol) converted after 3 h agree well with the amount of H₂ and CO₂ formed.

The results are not influenced by internal mass transfer according to the calculation of the Weisz Prater number as shown in the supporting information section internal mass transfer, as the estimated value is much lower than 1. However, we cannot rule out any effects of formation of bubbles in the catalyst pores, which might both slow down or enhance internal transport, the latter by causing chaotic movement of the liquid in the catalyst pore according to the “oscillation theory” [49–51]. Also, any influence of external mass transfer can be ruled out based on the observation that the stirring rate (above 375 rpm) has no influence on the reaction rate, as well as based on calculations, as shown in supporting information section on external mass transfer.

3.3. Effect of oxygen

Figure S2 in supporting information shows the conversion of formic-acid in time for experiments with oxygen concentrations between 0 and 2 vol%. Clearly, the presence of oxygen enhances conversion. Fig. 3a shows more clearly the effect of oxygen at low concentrations, i.e. below 0.1%. Fig. 3b shows that the initial apparent TOF increases with oxygen concentration between 0 and 2 vol% with almost a factor 3. However, the initial TOF is constant within experimental error at O₂ concentration below 0.1 vol %, in agreement with the fact that conversion seems independent of oxygen concentration during the first 30 min in Fig. 3a.

Fig. 4a shows the formic-acid conversion, and H₂ and CO₂ yields after three hours of reaction, calculated by integrating the H₂ and CO₂ concentrations in gas-phase as explained in section 3.2 and based on the final conversions shown in Figures 3 and S2. Fig. 4a shows that the hydrogen yield is maximal at 0.1 vol%. In contrast, the CO₂ yield increases with oxygen concentration until formic-acid is completely converted within 3 h. A similar trend in H₂ and CO₂ yield is also observed after 30 min reaction time as shown in Figure S3. Fig. 4a also shows that the CO₂ yield is always higher than the H₂ yield; the difference clearly increases with increasing oxygen concentration as shown in Fig. 4b. Figure S4 shows how that the ratio between H₂ yield and CO₂ yield decreases with reaction time in presence of 0.1% O₂, suggesting that the contribution of H₂ oxidation increases with time.

The mass balance in Fig. 4a is not completely closed and about 10% of the carbon seems lost, caused by the delay in the gas phase analysis data as discussed in Section 3.2. This is illustrated by Figure S5, showing that when formic-acid is completely decomposed, i.e. no further H₂ and CO₂ are produced, detection of H₂ and especially CO₂ in the gas phase continues for more than two hours. This is caused by slowly flushing out the gasses and the effect is much stronger for CO₂ because of the relatively high solubility of CO₂ in water. The accuracy of the carbon mass balance is probably most affected by CO₂ remaining in the water in the reactor.

Fig. 5 shows the formic-acid conversion profiles of an experiment in inert with an experiment under semi-inert conditions, i.e. by flushing only the gas-cap with inert gas without bubbling through the liquid. The red dots show 17% conversion in three hours under inert-experiment condition. In contrast, a much higher conversion (68%) is obtained under semi-inert conditions. The difference is caused by oxygen dissolved in the water as it is not removed with Ar under semi-inert conditions.

3.4. Effect of formic-acid concentration

Fig. 6 shows that the initial apparent TOF, in presence of 0.1 vol % oxygen, remains almost constant on changing the formic-acid concentration. Note that varying the initial formic-acid concentration between 2 and 10 mM also changed the initial solution pH.
between 3.2 and 2.9 [52]. As shown in Figure S6, the rate of reaction decreases with increasing pH, but the change within the pH window between 2.9 and 3.2 appears smaller than experimental accuracy. Therefore, it can be concluded that the apparent order in formic-acid is zero under our experimental conditions. Different reaction orders in formic-acid are reported in literature [20,23,53] but unfortunately the oxygen concentration was not well controlled in these studies. The importance of oxygen will be discussed later.

3.5. Catalyst stability

Catalyst stability was tested in both inert (Ar) as well as in the presence of 0.1 vol% O2. A single batch of the catalyst was tested during four hours by adding the same amount of the formic-acid every 60 min to the batch reactor. Fig. 7a shows the results under inert atmosphere. Clearly, formic-acid is almost fully converted in the first hour. The activity decreased significantly in the second hour after dosing additional formic-acid solution, and even more so after dosing for the third and fourth time. The catalyst clearly deactivates under inert condition. On the contrary, in the same experiments performed in 0.1 vol% oxygen, as shown in Fig. 7b, the catalyst maintained its activity in three runs, only showing mild deactivation in the fourth run.

Fig. 8 shows the formic-acid conversion profile after pretreatment of the catalysts with CO and standard inert experiment. Clearly, pretreatment with CO causes complete deactivation, which is confirmed by the observation that no gas products (H2, CO2, CO) could be detected with GC.

3.6. ATR experiments on formic-acid decomposition

Fig. 9 presents the ATR-IR spectra obtained with bare ZnSe, a bare alumina layer and a catalyst layer, exposed to formate solutions for at least 10 min at pH 3 and 5. The dark yellow line shows the spectrum on bare ZnSe at pH 5, showing three peaks at respectively 1581, 1380 and 1350 cm⁻¹. These three peaks are also observed in the experiments with the Al2O3 layer and the Pd/Al2O3 layer at different pH condition and are assigned to free formate in the bulk solution, in agreement with literature [18]. Note that the absolute intensities in Fig. 9 cannot be compared because the optical properties of the layers are different. The red line shows the spectrum obtained with Pd/Al2O3 at pH 5, showing an additional peak at 2350 cm⁻¹ which is assigned to CO2 [19,54–57], confirming the formation of CO2 via Pd-catalyzed formate decomposition. The black spectrum presents the result of the same experiment at pH 3, revealing both a larger CO2 peak at 2350 cm⁻¹ as well as a clear shoulder peak around 1610 cm⁻¹, which however...
spectrum shown in Fig. 9. Fig. 10b shows a zoom-in of the window between 1700 and 2200 cm\(^{-1}\) on the Pd surface \[30\], demonstrating the formation of adsorbed CO. The same experiment at pH 5 (Figure S7c) does not result in detection of CO during exposure to formic acid.

CO. The same experiment at pH 5 (Figure S7c) does not result in detection of CO during exposure to formic acid. The catalysts were used as prepared without any further pretreatment before the reaction, thus Pd and PdO co-exist initially. It is well known Pd\(^2+\) can be reduced to Pd\(^0\) metal state by formic-acid \[14,35,58,59\]. According to recent studies \[25,40\], in-situ reduction with H\(_2\) does not influence catalyst activity. In any case, any formic-acid consumption due to PdO reduction in our experiments can maximally convert 0.2% of the initial amount of formic-acid. So, this would not influence the catalyst activity.

4.2. Activity in inert atmosphere

As shown in Fig. 1, the catalyst is deactivated during the reaction when oxygen is absent, as only a small fraction of formic-acid is converted and the reaction rate is very small after two hours. The same is also observed in the experiment with repeatedly dosing of formic acid in Fig. 7a. Furthermore, the result shown in Fig. 8, obtained after pretreatment of the catalyst with CO, clearly demonstrates that CO deactivates the catalyst significantly, in agreement with claims in literature \[18,20,23–25,34,38,60\]. However, CO was never detected with GC, as CO absorbs very strongly on Pd and cannot desorb at room temperature. The amount of CO required to completely cover the Pd surface is as small as 3.2 * 10\(^{-3}\) mmol CO, which can be produced by dehydrogenation (Eq. (2)) of only 0.2% of the initial amount of formic-acid.

Formation of adsorbed CO during formic acid decomposition is confirmed by ATR-IR experiments in Fig. 10b. This agrees well with Jiang et al. \[18\], reporting similar results with ATR-IR. The peaks are slightly blue-shifted compared to our previous study \[30\], possibly caused by differences in pH, the surface coverage of CO or interaction with formate ions. Clearly, in-situ characterization is required to detect CO as ex-situ IR spectroscopy failed as reported by Hu et al. \[25\], probably caused by oxidation of adsorbed CO in air.

In previous studies, TOFs were calculated based on the production rate of H\(_2\) \[14,23,31,53,61\] or total gas production rate (H\(_2\) and CO\(_2\)) \[25,36,37\], resulting in TOFs typically between 100 and 1000 h\(^{-1}\). Unfortunately, the level of conversion is not reported, making direct comparison impossible. On top of that, the presence of oxygen was not clearly reported, which is important as will be discussed below.

Table 3 summarizes the results of studies performed in well-controlled inert atmosphere. Clearly, the initial apparent TOF in our work is in the same order of magnitude or somewhat larger as reported in literature \[42,62–64\], despite differences in precise conditions and uncertainty about any undesired effect of mass transfer, except for our data. The fact that high TOF is observed at low formic-acid concentration is in line with the order zero in formic-acid (Fig. 6), also confirming that formic-acid mass transfer cannot be limiting in our experiments.

4.3. Influence of pH

The activity of the Pd catalyst decreases with increasing pH, independent of the oxygen concentration as shown Figure S6 in presence of 0.1 vol% O\(_2\) and under inert conditions. This agrees well with the observations in ATR-IR experiments that both CO\(_2\) and adsorbed CO form faster at pH 3 (Fig. 10) than at pH 5 (Figure S7). The results suggest that un-dissociated formic acid rather than formate ions react, but this observation can also be interpreted in terms of the electrochemical potential of the Pd particles, which decreases with increasing pH.

Many reports in literature \[20,36,39\] report on the influence of the ratio of formic-acid and sodium-formate in the reaction mixture, without considering that the actual concentration of formate-ions is determined by the acid-base equilibrium of the
dissociation of formic-acid (Eq. (8)) as also argued for the first time in [53].

\[
\text{HCOOH} \rightarrow \text{HCOO}^- + \text{H}^+ \tag{8}
\]

The consequence is that the reactant concentration, i.e. the sum of formate and formic acid, is not constant so that an unambiguous observation on the effect of pH on the reaction rate is not obtained. Nevertheless, the qualitative observation that basic solutions result in very low reaction rates, is in agreement with observations in literature [32,36,39,53,65].

4.4. Activity in presence of oxygen

Fig. 3b shows that the apparent initial TOF increases with increasing oxygen concentration, although the effect is insignificant when varying the oxygen concentration in a narrow window between 0 and 0.1 vol%. Fig. 3a shows that the catalyst activity remains higher during the experiment on increasing the oxygen concentration, achieving much higher conversion. In other words, catalyst deactivation is suppressed by oxygen, even if the oxygen concentration is very low, i.e. below 0.1 vol%. The result in Fig. 7b confirms that catalyst stability is significantly improved by introducing trace amounts of oxygen. However, it is also clear that deactivation occurs in the fourth run, suggesting that a second deactivation mechanism is in operation. In any case, low oxygen concentration improves stability of Pd catalysts for formic-acid decomposition.

Oxygen may be involved in three reactions as presented in Scheme 1, all leading to formation of H$_2$O and CO$_2$. Firstly, oxygen may react with CO to form CO$_2$ (step 4), termed as CO oxidation. Secondly oxygen may oxidize H$_2$ to H$_2$O (step 3), termed as H$_2$ oxidation, which are both consecutive reactions. Thirdly, formic-acid may react directly (step 6) with oxygen dissociated on the Pd surface (step 5), termed as formic-acid oxidation.

The effect of small concentrations of oxygen on catalyst performance is attributed to step 4, decreasing the CO coverage of the Pd surface and suppressing or even preventing deactivation, as is argued below.

In principle, the conversion rate of formic-acid could also be boosted via the reaction in step 5 and 6, i.e. direct deep oxidation...
of formic-acid. There are three arguments against this proposition. Firstly, if steps 5 and 6 would take over completely after one hour in the experiment with 0.1 vol% O₂ (see Fig. 3a), i.e. forming CO₂ and H₂O exclusively during the second and third hour, the H₂/CO₂ ratio would decrease from 0.73 (Figure S4) after 1 h to 0.32 after 3 h. However, the observed H₂/CO₂ ratio after 3 h is 0.58 (Figure S4), implying that H₂ formation via reaction (1) continued during the whole experiment. Note that the H₂/CO₂ ratio is calculated based on the integral amounts of the H₂ and CO₂ produced. Secondly, the H₂ yield increases with increasing oxygen concentration below 0.1 vol% as can be seen in Fig. 4a and S3b, implying that H₂ formation rate increases over the whole experiment. Thirdly, the presence of a very small amount of O₂ in the reactor, i.e. by removing oxygen only in the gas cap before the experiment and leaving dissolved oxygen in water behind (Fig. 5), increases the conversion after 3 h from 17% (in inert conditions) to 68%. Stoichiometric reaction of O₂ dissolved in water in equilibrium with air could account for an increase in conversion of maximal 11%. The real contribution is even smaller because the oxygen concentration in water will decrease somewhat during flushing the gas cap with inert gas.

![Fig. 10. a) ATR-IR spectra of formic-acid decomposition at pH = 3 flowing for 5 min, b) zoom-in a) in the window of 1700 and 2300 cm⁻¹ (5 mg 1 wt% catalyst on ZnSe, 10 mM formic-acid solution, 0.5 mL/min flow rate).](image)

**Table 3**

| Catalyst                  | Temperature | Formic-acid concentration | pH   | Pd metal size | Support size | TOF          |
|---------------------------|-------------|---------------------------|------|---------------|--------------|--------------|
| Pd/C [42]                 | 20–25 °C    | 1000 mM                   | 1.88 | 1.9–3.2 nm    | N.A.         | 60–100 h⁻¹   |
| Pd/H-BETA(0.5) [62]       | 50 °C       | 1000 mM                   | 1.88 | 3.4 nm        | N.A.         | 59.2 h⁻¹     |
| Pd/SiO₂ [63]              | 30 °C       | 1000 mM                   | 1.88 | 3.5 nm        | N.A.         | 23.4 h⁻¹     |
| Pd/g-C₃N₄ [64]            | 30 °C       | 1000 mM                   | 1.88 | 4.6 nm        | N.A.         | 35 h⁻¹       |
| This work                 | 20 °C       | 5 mM                      | 3    | 2.8 nm        | Below 20 μm  | 230 h⁻¹      |

**Scheme 1.** Formic-acid decomposition reactions under oxygen condition.
These three observations demonstrate that preventing deactivation via removal of adsorbed CO by oxidation is the dominant mechanism, whereas any effect via direct oxidation of formic acid is minor.

It should be noted that no distinction is possible between “direct oxidation of formic acid (5 and 6)” and the combination of “dehydrogenation followed by $\text{H}_2$ oxidation (1 and 3)” and “decomposition followed by CO oxidation (2 and 4)”. Therefore, the same arguments discussed above could also be used to show that CO oxidation dominated over $\text{H}_2$ oxidation at $\text{O}_2$ concentration up to 0.1%.

On the other hand, the situation is quite different at higher $\text{O}_2$ concentrations, where step 3 and/or 6 clearly dominate, decreasing the $\text{H}_2$ yield, as shown in Fig. 4a. It is clear that oxygen not only suppresses deactivation, but also influences the rate of conversion of formic acid by opening an additional reaction pathway, influencing also the product distribution.

There are three types of experiments reported in literature for studying formic acid decomposition. First, in many studies the experiments were conducted in air, implying that oxygen is present in both the gas above the solution as well as in the solution [16,18,20,23,25,31–37,39,40,60,61,66–69]. Second, in some studies the air above the solution was removed by flushing with inert before the reaction was initiated, implying that oxygen dissolved in the liquid might still be present [19,53,70–72]. This is the same, somewhat poorly defined, situation as we applied in Fig. 5, demonstrating a strong influence on the reaction rate. Third, in a few studies air was completely removed from the reactor including the solution, which is the standard method in this study [24,41,42,62–64,73,74]. The results confirm that Pd catalysts deactivate [24,41,64,73], in agreement with our results in inert. Our study shows not only that presence of oxygen at low concentration, i.e. 0.1%, suppresses catalyst deactivation, but also that the observed reaction rates are strongly influenced by the presence of oxygen in the concentrations window between 0.2 and 2%. Therefore, the effect of oxygen should be rigorously considered in future research on efficient catalysts for formic acid decomposition.

From a practical point of view and considering formic acid as a possible way to store hydrogen, efficient recovery of hydrogen by formic acid decomposition is important. This efficiency can be calculated based on the integral $\text{H}_2/\text{CO}_2$ ratio, as $\text{CO}_2$ is the only C-containing product detected and the amount of chemisorbed CO can be neglected. The data in Fig. 4b show that the efficiency is 90% in the absence of any oxygen, whereas the apparent loss of 10% is assigned to $\text{CO}_2$ staying behind in the reactor dissolved in water, as discussed in Section 3.3. In any case, the efficiency decreases to 58% in the presence of 0.1% of oxygen. Consequently, addition of traces of oxygen can prevent deactivation, but only with the disadvantage that efficiency decreases significantly. Further research would be required to solve this problem.

5. Conclusion

The kinetics of formic acid decomposition over Pd catalyst supported on alumina is strongly influenced by deactivation during the batch experiment, dominantly caused by CO poisoning. Deactivation can be suppressed by dosing trace amounts of oxygen. However, oxygen reacts not only with adsorbed CO, preventing deactivation, but also with $\text{H}_2$ simultaneously. Operation at oxygen concentrations below 0.1 vol% enhances the production of hydrogen, as efficient prolonging catalyst activity dominates over consecutive oxidation of hydrogen. Furthermore, oxygen concentrations between 0.1 vol% and 2 vol% cause significant increase in the rate of conversion of formic acid and influences also the product distribution, i.e. decreasing the hydrogen yield, which in many cases is not accounted for in reported batch experiments on Pd catalyzed decomposition of formic acid in literature.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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