Numerical Modeling of Hydroperoxyl–Mediated Oxidative Dehydrogenation of Formic Acid under SCR–Relevant Conditions

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Abstract

Formic acid decomposition to carbon dioxide is an important step during the decomposition of alternative formate-based ammonia precursor compounds, such as ammonium formate, guanidinium formate and methanamide in the selective catalytic reduction (SCR) process. At oxygen and water concentrations prevalent in a typical SCR feed, an oxidative dehydrogenation (ODH) type pathway of formic acid decomposition proceeds on titania-supported gold catalysts. Using the surface perfectly stirred reactor (SPSR) model, the ODH mechanism is demonstrated to satisfactorily predict the experimentally observed conversions. The single-site mechanistic model captured the negative trend in conversion with increasing formic acid concentrations, stemming from an extensive coverage of the active sites by formates. This in turn rendered the active sites unavailable for the formation of the active hydroperoxyls required for the rate determining step of C-H bond scission of formates. The positive order dependency on oxygen concentration and the promotional effect of water are quantitatively and semi-qualitatively described by the model. Predicted trends in the relative surface coverages of different reaction intermediates are in agreement with previously reported kinetic and spectroscopic measurements. These results are important fundamentally for the understanding of formic acid decomposition chemistry and general catalysis by gold, as well as for the design of dedicated hydrolysis catalysts for applications in the SCR process.

Keywords: Oxidative dehydrogenation of formic acid, titania-supported gold catalyst, hydroperoxy species, surface perfectly stirred reactor, sensitivity analysis

1. Introduction

Formate-based ammonia precursors are promising alternatives to urea in SCR applications owing to their favorable properties, namely, lower freezing point, higher ammonia storage capacity and higher thermal stability and durability [1–7]. Considering that many of these precursors release formic acid upon thermolysis in the hot diesel engine exhaust [8,9], their successful application in the SCR process requires rapid and selective decomposition of formic acid to carbon dioxide to prevent side-product formation and suppress formic acid emission. In this context, titania-supported gold catalysts show excellent activity and selectivity to decompose formic acid to carbon dioxide under the highly oxidizing conditions relevant to SCR [10]. Importantly, the catalysts did not catalyze ammonia oxidation, which is highly desirable since the latter is required for the SCR process. Under the investigated conditions in [10], which are similar to those prevalent in the engine exhaust, formic acid decomposes to carbon dioxide and carbon monoxide. The addition of lanthana to the catalyst formulation resulted in the selective enhancement in the carbon dioxide production rates, while carbon monoxide formation was suppressed [11]. It is known that, instead of direct formic acid oxidation to carbon dioxide, formic acid could alternatively first decompose to carbon monoxide as an intermediate that subsequently oxidizes to carbon dioxide [12,13]. Further experiments revealed that carbon monoxide oxidation was irrelevant for the formic acid decomposition mechanism on the unmodified and lanthana-modified gold catalysts and that the lanthana-induced rate enhancement was caused only by acceleration of the direct oxidative decomposition pathway to water and carbon dioxide [11].

Kinetic and mechanistic investigations revealed that carbon dioxide and carbon monoxide formation from formic acid decomposition proceed as two independent reactions occurring on two different active sites: the former associated with gold and the latter exclusively with the support. Excess oxygen and water, present in the exhaust feed, influenced the kinetics of the two reactions differently. On the one hand, oxygen was mandatory for carbon dioxide production on gold. A synergy between oxygen and water led to higher carbon dioxide production rates, similar to the promotional effect of water [14–16] in oxygen activation during carbon monoxide and alcohol oxidation on gold. On the other hand, carbon monoxide formation occurring on titania was unaffected by the presence or absence of oxygen. Water suppressed the carbon monoxide formation rates as opposed to the promotional effect on carbon dioxide production.

Based on the in-depth kinetic and in situ DRIFTS analyses, a mechanism was proposed in which the formation of hydroperoxy species via a proton shift equilibrium between adsorbed oxygen and water bypassed the energetically intensive step of oxygen activation on gold [17–24]. The rate-determining step involved the C–H bond scission of the abundantly present formate species with the aid of hydroperoxy species to form carbon dioxide and water. The proposed ODH mechanism induces reaction orders that are consistent with the experimentally observed conversions. This mechanism, describing an ‘oxidative dehydrogenation’ (ODH) type pathway for formic acid conversion to carbon dioxide and water under highly oxidizing and wet conditions simulating the exhaust feed, is markedly different from the stoichiometric formic acid decomposition or formate dehydrogenation to carbon dioxide and hydrogen that are often studied in the context of hydrogen generation in fuel cells and the water gas shift reaction [25–28].

As a next step, it is essential to numerically model this mechanism to test its applicability in predicting the observed catalytic performance. The surface perfectly stirred reactor (SPSR) is a widely applied model to successfully simulate complex reaction networks involved in homogeneous fuel combustion as well as in catalytic emission control [29–39]. For instance, Chaniotis and Poulikakos used an SPSR to validate the kinetic model describing the catalytic partial oxidation of methane in a fuel cell [35]. Mantzaras and coworkers performed sensitivity analysis in an SPSR to investigate the influence of surface chemistry on the oxidation of carbon monoxide in carbon monoxide/hydrogen/air mixtures [31] and on hetero-/homogeneous combustion of methane/air [36] and ethane/air mixtures [33] over platinum, all under fuel-lean stoichiometries. In the SPSR, the contents of the reactor are assumed to be nearly spatially uniform owing to high diffusion rates or forced turbulent mixing. Thus, the rate of conversion of reactants to products is considered to be controlled by chemical reaction rates and not by mixing processes. The crucial element of the SPSR is its underlying assumption that sufficient mixing allows it to be described well by spatially averaged or bulk properties. The main advantage of such an approximation lies in the relatively small computational demand of the mathematical model. Further information of the SPSR model can be found in the reference [40]. In this work, the validity of the proposed ODH mechanism is tested by comparing SPSR model predictions with the experiments on gold supported on lanthana-modified titania. An estimate of the relative coverages of the different reaction intermediates is provided and sensitivity analyses are performed to determine the dominant elementary steps controlling the conversion of reactants.

2. Experimental

Catalyst preparation, testing and kinetic measurements. The preparation and testing of the titania-supported gold catalyst modified with lanthana can be found elsewhere [11,41,42]. In brief, titania anatase modified with 10 wt % lanthana (DT57, Crystal Global) was impregnated with a 0.032 M solution of HAuCl₄ (Sigma–Aldrich). Aging and washing with aqueous ammonia solution and distilled water, in that order, was followed by calcination at 400 °C for 5 h in air. The base–modified catalyst was designated as Au/La–TiO₂. The catalyst was coated on cordierite monoliths at a desired washcoat loading of ~2.5 g L⁻¹ and tested in a laboratory reactor dedicated to investigating the interaction of catalyst-coated monoliths with sprayed liquid solutions [41]. Gaseous products at the reactor outlet were quantified by FTIR spectroscopy (Antaris, Thermo Nicolet) [42]. The total flow rate was set at 750 L h⁻¹ and the contact time was varied by changing the number of monoliths stacked along the length of the reactor, while keeping constant the total catalyst concentration per unit volume. Concentrations of formic acid, oxygen, and water in the feed were varied in the range between 227 and 1070 ppm (see Table 1). External and internal mass transfer limitations were ruled out [11] which, together with the isothermal operation, facilitated the applicability of the SPSR model. The SPSR tool was indispensable due to the large number (~5,000) of optimization simulations. The formulae used for the calculation of conversion, product selectivity and yield are described in our previous work [11]. The C–balance was closed within an accuracy of ±3% by summing up carbon monoxide, carbon dioxide and formic acid. Temperature programmed oxidation and time-on-stream experiments revealed that no carbon deposition occurred on the catalysts.

Table 1. Experimental conditions^a

Case	Formic acid	Oxygen	Water	Temperature
	(mol/mol)	(mol/mol)	(mol/mol)	(°C)
I	0.00065	0.1	0.05	160–300
II	0.000227–0.00107	0.1	0.05	200, 300
III	0.00065	0.0025–0.03	0.05	200, 300
IV	0.00065	0.1	0.005–0.013	200, 300

^a The feed was diluted with nitrogen to achieve a total flow of 750 L h⁻¹, contact time (W/F) = 2.4·10⁻⁵ g s cm⁻³.

Mechanistic model. The proposed mechanism for the ODH of formic acid under SCR-relevant conditions encompasses 16 reactions out of which 14 represent the forward and backward direction of seven fast and quasi-equilibrated elementary reactions [43]. The remaining two steps involve the slow and irreversible steps of hydrogen abstraction from the adsorbed formate with the aid of activated oxygen species. Table 2 lists the 16 surface reactions and values for the Arrhenius pre-exponentials, temperature exponents and the activation energies. HCOO*, HOO*, H₂O*, O₂*, O*, HO* and H* describe the surface intermediates adsorbed on the active site '*'. Coverage-dependent activation energies (COV) were introduced for steps 9 and 10. This mechanistic scheme does not take into account the formic acid decomposition to carbon monoxide on titania and to carbon dioxide in the gas phase, because their contributions are very low [11]. Methodologies for microkinetic surface mechanism development with thermodynamic (enthalpic and entropic) consistency have been put forth (Mhadeshwar et al. [44]). Nonetheless, such a rigorous approach was not followed herein, as it is best suited when basic knowledge on kinetic parameters is available (e.g. estimates of activation energies via DFT calculations, estimates of pre-exponentials via transition state theory-TST, experimental input via TPD etc.). Thermodynamic consistency is less important in the present application. For example, enthalpic inconsistency leads to incorrect solutions of the energy equation and this is important in non-isothermal simulations. However, the present model is isothermal (as also a practical SCR system is) such that no energy equation is solved. Furthermore, conditions are away from equilibrium since the residence times in the simulations are quite short (~12 ms).

Numerical model. The numerical platform for the kinetic studies is the steady-state SPSR model [40]. The salient features of this model include perfect mixing and spatially uniform temperatures and species compositions. In this zero-dimensional model, the inlet species undergo instantaneous homogeneous mixing such that only kinetic limitations are present [40]. Simulations are carried out at a fixed SPSR temperature (mimicking the present isothermal reactor experiments), thus negating solution of the energy equation. The gas-phase species governing equations for a steady state SPSR in the presence of catalytic and gas phase reactions are:

$$\dot{m} (Y_{k,OUT} - Y_{k,IN}) = V \dot{\omega}_k W_k + S \dot{s}_k W_k, \quad k = 1, 2, \dots, K_g, \quad (\text{Eq. 1})$$

where $\dot{m}$ is the mass flow rate in the reactor in g/s, $Y_{k,IN}$ and $Y_{k,OUT}$ the mass fractions of the k -th gaseous species at the inlet and outlet, respectively, $\dot{\omega}_k$ the volumetric molar production rate of k -th species via gaseous reactions in $\text{mol}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$, $\dot{s}_k$ the surface molar production rate of k -th species via catalytic reactions in $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, S and V the SPSR surface area (cm^2) and volume (cm^3), respectively, W_k the molecular weight of the k -th species in $\text{g}\cdot\text{mol}^{-1}$, and K_g the total number of gas phase species. In the present case $K_g = 5$, accounting for formic acid, oxygen, water, carbon dioxide and nitrogen. The gaseous reaction rates $\dot{\omega}_k$ in Eq. 1 have quite small contributions at the present moderate temperatures and are thus neglected. The known variables are $\dot{m}$, $Y_{k,IN}$, S , W_k and $\dot{s}_k$, where $\dot{s}_k$ are calculated from the forthcoming Eq. 3.

Table 2. Sequence of steps describing ODH of formic acid on Au/La-TiO₂ and their corresponding kinetic parameters^a

Step	Elementary steps	A ($\text{mol}\cdot\text{cm}\cdot\text{s}$)	b	E_{act} (kJ mol^{-1})
1	$\text{H}_2\text{O} + * \rightarrow \text{H}_2\text{O}^*$	1.20E+18	0.0	52.0
2	$\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O} + *$	8.50E+14	0.0	110.0
3	$\text{O}_2 + * \rightarrow \text{O}_2^*$	1.04E+17	0.0	60.0
4	$\text{O}_2^* \rightarrow \text{O}_2 + *$	1.00E+15	0.0	120.0
5	$\text{H}_2\text{O}^* + \text{O}_2^* \rightarrow \text{HOO}^* + \text{HO}^*$	1.60E+21	0.0	50.0
6	$\text{HOO}^* + \text{HO}^* \rightarrow \text{H}_2\text{O}^* + \text{O}_2^*$	1.20E+22	0.0	50.0
7	$\text{HCOOH} + \text{HO}^* \rightarrow \text{HCOO}^* + \text{H}_2\text{O}$	1.42E+26	0.0	38.0
8	$\text{HCOO}^* + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{HO}^*$	5.25E+18	0.0	30.0
9	$\text{HCOO}^* + \text{HOO}^* \rightarrow \text{CO}_2 + \text{H}_2\text{O} + * + \text{O}^*$	1.70E+13	0.0	$32.3 + 3.65\theta_{\text{HCOO}^*}$
10	$\text{HCOO}^* + \text{O}^* \rightarrow \text{CO}_2 + \text{HO}^* + *$	2.50E+20	0.0	$25.8 + 1.46\theta_{\text{HCOO}^*}$
11	$2\text{HO}^* \rightarrow \text{H}_2\text{O}^* + \text{O}^*$	2.00E+20	0.0	40.0
12	$\text{H}_2\text{O}^* + \text{O}^* \rightarrow 2\text{HO}^*$	2.00E+20	0.0	60.0
13	$\text{H}_2\text{O}^* + * \rightarrow \text{HO}^* + \text{H}^*$	1.55E+22	0.0	40.0
14	$\text{HO}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* + *$	2.40E+21	0.0	30.0
15	$\text{H}^* + \text{O}^* \rightleftharpoons \text{HO}^* + *$	2.30E+22	0.0	40.0
16	$\text{HO}^* + * \rightarrow \text{H}^* + \text{O}^*$	2.0E+22	0.0	40.0

^a The rate constant, k , is given by $k = A \cdot T^b \cdot e^{\frac{-E_{act}}{RT}}$, with $b = 0$. θ_{HCOO^*} is the surface coverage of adsorbed formate. The kinetic parameters of steps 1-4 have been adjusted, based on values from references [45–47].

The coverage equations for the surface species are given by:

$$\frac{\partial \theta_m}{\partial t} = \sigma_m \frac{\dot{s}_m}{\Gamma}, \quad m = 1, 2, \dots, K_s. \quad (\text{Eq. 2})$$

The left-side in Eq. 2 is not a true transient term and is only introduced to facilitate numerical convergence to steady state; therein, limited time integrations may be performed to bring the solution within the convergence domain of the employed Newton solver [40]. In Eq. 2, σ_m is the site occupancy (number of sites occupied by the m -th surface species), Γ the surface site density, θ_m the surface coverage of the m -th species and K_s the total number of surface species. In the present case $K_s = 8$, which accounts for HCOO^* , HO_2^* , HOO^* , O_2^* , O^* , HO^* , H^* and $*$ (the latter denotes the available free sites). The value of σ_m is unity since each surface species occupies only one site. Since the value of Γ for gold is not known, the corresponding value for platinum [48] (equal to $2.7 \times 10^{-9} \text{ mol cm}^{-2}$) is employed. The surface reaction rates are given by:

$$\mathfrak{R}_m = \sum_{l=1}^{N_s} \nu_{ml} k_{f_l} \prod_{j=1}^{K_g+K_s} C_j^{\nu'_{jl}}, \quad (\text{Eq. 3})$$

with N_s the number of surface reactions and $\nu_{m\ell}$ the stoichiometric coefficient of species m in surface reaction λ . For the gas phase species ($j = 1, 2, \dots, K_g$) the concentrations in Eq. 3 are $C_j = \rho Y_j / W_j$ (mol/cm^3), while for the surface species ($j = K_g+1, K_g+2, \dots, K_g+K_s$) the corresponding surface concentrations are $C_j = \Gamma \theta_j / \sigma_j$ (mol/cm^2). The reaction rate coefficients k_{f_ℓ} in Eq. 3 are:

$$k_{f_l} = A_l T^{\beta_l} \exp\left(\frac{-E_l}{RT}\right) \prod_{m=1}^{K_s} \theta_m^{\mu_{ml}} \exp\left(\frac{\varepsilon_{ml} \theta_m}{RT}\right), \quad (\text{Eq. 4})$$

with A_ℓ , β_ℓ and E_ℓ the pre-exponential, temperature exponent, and activation energy of surface reaction λ , respectively. The parameters $\varepsilon_{m\ell}$ and $\mu_{m\ell}$ describe coverage dependencies of the reaction rate coefficient, which account for variation in the adsorption binding states due to changing surface coverage [49]. In the present mechanism $\mu_{m\ell} = 0$ for all surface reactions, while $\varepsilon_{m\ell}$ is non-zero only for reactions 9 and 10 for the surface formate HCOO^* .

Equations 1 and 2 constitute a system of non-linear algebraic equations, solved by a modified Newton method for the unknown mass fractions $Y_{k,OUT}$ of gas-phase species and surface coverages θ_m [40]. The computed $Y_{k,OUT}$ in turn yield the % species conversions,

$K_k = 100(Y_{k,IN} - Y_{k,OUT})/Y_{k,IN}$. In Newton's method, a sequence of iterations is followed, each successively approaching the true solution. For the sake of brevity, the approximate solution vector at a given iteration is called $\vec{\varphi}$. When $\vec{\varphi}$ is inserted into the governing equations, the equations are satisfied within a residual vector $\vec{F}$. The objective then is to find a solution $\vec{\varphi}$ such that $|\vec{F}(\vec{\varphi})| \leq \varepsilon$, with a herein selected $\varepsilon = 10^{-20}$. A more detailed overview of this approach can be found in reference [40].

The sensitivity coefficients ($SC_{i,\ell}$) for the conversion of species i (being either formic acid, oxygen or water) on reaction λ are calculated as follows:

$$SC_{i,\ell} = \frac{A_\ell}{K_{i,A_\ell}} \frac{K_{i,A_\ell+\delta A_\ell} - K_{i,A_\ell}}{\delta A_\ell}, \quad (\text{Eq. 5})$$

where A_ℓ is the pre-exponential of the λ -th reaction, δA_ℓ the change in the pre-exponential (always 2% increase of A_ℓ), K_{i,A_ℓ} is the conversion of species i when the pre-exponential is A_ℓ , and $K_{i,A_\ell+\delta A_\ell}$ the conversion of species i when the pre-exponential is $A_\ell + \delta A_\ell$.

The SPSR simulates a single channel of the honeycomb reactor used in the experiments. The geometrical parameters of a single honeycomb channel yield an area $S_{\text{chan}} = 0.5786 \text{ cm}^2$, while the mass flow rate $\dot{m}_{\text{chan}}$ is calculated by dividing the total honeycomb mass flow rate by the number of channels (159). Geometrical and flow properties of each channel are calculated as follows:

- Honeycomb type: 400 cpsi (cells per square inch), length $L = 1.45 \text{ cm}$.
- Total number of cells in honeycomb: 159 cells
- Total flow rate is 750 L/h at STP (273.15 K and 1 bar), equivalent to $208.33 \text{ cm}^3/\text{s}$ at STP. For each channel, the flow rate is $Q_{\text{chan}} = 1.313 \text{ cm}^3/\text{s}$ at STP.

Density of feed mixture (10% O_2 , 5% H_2O , 85% N_2) at STP is $1.23 \times 10^{-3} \text{ g/cm}^3$ and the mass flow rate in each channel is in the range $0.001680 \leq \dot{m}_{\text{chan}} \leq 0.001682 \text{ g/s}$.

- The equivalent diameter of each channel is $d_{\text{chan}} = 0.127 \text{ cm}$ and the volume of each channel is $V_{\text{chan}} = (\pi d_{\text{chan}}^2/4)L = 0.018368 \text{ cm}^3$.
- Surface area of each channel is $S_{\text{chan}} = \pi d_{\text{chan}} L = 0.5786 \text{ cm}^2$.

3. Results and Discussion

3.1. Case I: Effect of temperature at fixed feed composition

Figure 1 compares model predictions with the experimental formic acid conversion for Case I (Table 1). The catalyst exhibited a typical Arrhenius behavior. The proposed mechanistic model yielded good agreement between the experimental and predicted conversions. The small deviation in the predictions at low temperature may be inherent to the homogeneous contribution [9] that is neglected in the proposed heterogeneous scheme.

Figure 1. Comparisons of predicted and measured formic acid conversions as a function of temperature for Case I, Table 1.

Figure 2 depicts surface coverages of the eight reaction intermediates involved in the ODH of formic acid as a function of reaction temperature. An increase in temperature entailed an increase in the surface coverages of molecularly as well as atomically adsorbed oxygen species. This agrees well with the strongly activated nature of these reactions [50–53]. Mantzaras and coworkers reported a similar behavior, wherein the coverage of the atomically adsorbed oxygen species increased monotonically with increasing wall temperature during platinum–catalyzed carbon monoxide oxidation in a channel–flow reactor [31]. Formates and hydroperoxyls, which dominate the surface at all temperatures, followed inverse trends. The lower formate coverages at higher temperatures can stem from two phenomena: (a) increased availability of activated oxygen species, which promote more rapid consumption of formates to produce carbon dioxide, (b) higher formic acid desorption rates. Complementary to the fall in the formate coverage, the proportion of free active sites experienced a slight increase with increasing temperature. Such a trend is in line with the in situ DRIFTS results [11,43], which

showed lower steady state formate coverages at higher temperature. The formation of hydroperoxyls (step 5, Table 2) is favored at higher temperature [54], as evidenced from an increased coverage of these species. The reduced coverage of adsorbed hydrogen species with increasing temperature up to 260 °C could arise from increased rates of reaction with atomically adsorbed oxygen species to form hydroxyl, which in turn could capture more adsorbed hydrogen to form water (as discussed next). The adsorption–desorption equilibrium for water shifts towards desorption with increasing temperature leading to a decreasing water coverage [55]. The coverage of hydroxyls, which are involved in multiple reaction steps, undergoes very little change with varying temperature. The low site occupancy of these species is in agreement with their high degree of depletion observed using in situ DRIFTS [43].

Figure 2. Predicted surface coverages as a function of temperature for Case I, Table 1.

Interestingly, the model predicts relatively higher coverages of hydroperoxy species than formates at higher temperature (300 °C), even though formic orders were still negative and the oxygen/water orders were positive [43]. While, there is a small probability that the active sites are only ‘kinetically saturated’ [56] by formates and that they do not necessarily physically represent the majority of surface species on the active sites, it is also important to note that the predicted trends in the surface coverages may be indicative as a result of the adopted kinetic parameter optimization (Table 2). Within the timeframe of this study, the current predictions make up the best match to the experiments.

Figure 3. Reaction flux diagram for Case I, Table 1 at 300 °C. Thicker lines (not to scale) denote dominant reactions. Units are in mol/cm²/s.

Figure 3 presents a reaction flux diagram for Case I, computed at 300 °C. The initiating steps were molecular adsorption of oxygen (net of R3-R4), water (net of R1-R2) and the Eley–Rideal–type reaction of formic acid with adsorbed hydroxyl to form surface formate (net of R7-R8). The main surface steps were the Langmuir–Hinshelwood type reactions of adsorbed oxygen and water to form the hydroperoxyl (net of R5-R6), which in turn reacted with adsorbed formate to form carbon dioxide and an atomically adsorbed oxygen species (R9). The latter reacted with another formate to form another carbon dioxide molecule and an adsorbed hydroxyl (R10). Other flux analyses indicated that the dominant pathways remained essentially the same at 200 °C (not shown), except that the net rates were about one order of magnitude lower. The net rate of formate formation was about twice as high as that of oxygen and water adsorption, indicating that the former step was more favored leading to high formate coverages (Figure 2). Consequently, the catalytic rate was controlled by the hydroperoxyl–assisted decomposition of abundantly present formates. Similar trends were observed for carbon monoxide oxidation on a platinum surface, where the high sticking coefficient of carbon monoxide dominated the slower oxygen adsorption and activation steps and resulted in lower catalytic rates despite the abundance of oxygen in the gas phase [31].

Figure 4 presents the sensitivity coefficients (see Eq. 5) for the conversion of formic acid, oxygen and water at 300 °C and 200 °C. A positive coefficient indicates that a given reaction step promotes the species conversion and, conversely, a negative coefficient signifies an

inhibiting effect of the step. The three reactants showed similar trends in sensitivities, indicating that formic acid, oxygen and water reacted with one another in a common pathway to form carbon dioxide. At 300 °C, the rate-determining-step of hydroperoxyl-mediated dehydrogenation of formate to carbon dioxide and water (step 9, Table 2) predominantly controlled the conversion of all reactants (Figure 4, top row). However, a slightly different picture appeared at 200 °C (Figure 4, bottom row). The high formate coverages at the low temperature (Figure 2) inhibited further consumption of the reactants, which was reflected in the form of highly negative coefficients for the step of formate formation (step 7, Table 2). Contrarily, the formate desorption to molecular gas phase formic acid (step 8, Table 2), which freed up active sites, promoted the conversion of all reactant species. This was consistent with the observations of Zheng et al. [31] on platinum on which carbon monoxide adsorption was found to inhibit its own consumption as well as the oxygen consumption for surface temperatures below 280 °C. Thus, the proposed single-site mechanism correctly describes the effects of competitive adsorption between formic acid, oxygen and water, where the rate of reactant consumption is impeded by the poisoning of active sites by formates.

Water and oxygen adsorption showed opposing effects, wherein the former (step 1, Table 2) inhibited and the latter (step 3, Table 2) promoted the conversion of reactants. Furthermore, water dissociation to adsorbed hydroxyl and hydrogen (step 13, Table 2) suppressed the conversion. This could be explained by considering that an increasing hydroxyl concentration further promoted the Eley-Rideal reaction with formic acid to form surface formate (step 7, Table 2), which in turn inhibited the conversion.

Figure 4. Sensitivity analysis for conversion of formic acid, oxygen and water, in a surface perfectly stirred reactor (SPSR) for Case I, Table 1 at 300 °C and 200 °C. Reaction numbering follows Table 2.

3.2. Effect of feed composition on the catalytic activity and the relative surface coverages of intermediates

3.2.1. Case II: Varying the formic acid concentration

Figure 5 plots the trends in the measured and predicted formic acid conversion as a function of gas-phase formic acid concentration at 200 °C and 300 °C. By imposing coverage-dependent activation energies of the rate determining steps, the proposed mechanism was able to essentially capture the negative trend in conversion with increasing formic acid concentration. The coverage-dependent activation energies are supported by the experimentally observed increase in the activation energy with increasing formate coverage on the active sites [11]. In our previous work [43], the inhibitory effect on conversion was attributed to the strong surface poisoning by formates, which in turn reduced the availability of active sites for the adsorption and formation of the activated oxygen species necessary for formate decomposition.

Although the results of the numerical simulations are in satisfying agreement with the experimental values there is still room for improvement since there is a noticeable difference from the measured values at 300 °C. One possible explanation for the deviation at 300 °C is that the proposed scheme considers only one type of active site that can adsorb formic-derived species (formates) and produce carbon dioxide. However, as shown in our previous works [11,43], other sites exist on the support away from the gold, which deprotonate formic acid and decompose the formate to carbon monoxide. These carbon monoxide-producing sites exhibited formic acid orders ranging between 0.0 and 0.5 suggesting that they harbor formate coverages equal to or lower than the saturation coverage. Since this pathway is not integrated into the mechanistic model, higher formate coverages on the carbon dioxide-producing active sites are anticipated by the mechanistic model at a given formic acid concentration than those existing in reality. Hence a higher degree of surface poisoning by formates can account for lower predicted formic acid conversion. Such an explanation is in line with the close agreement observed at 200 °C in Figure 5. The formate coverage at the carbon monoxide producing sites on the support was negligibly low at this temperature owing to competitive adsorption and site blockage by water as shown in our previous works [11,43]. Thus, at such temperature, the actual formate coverage on the carbon dioxide producing active sites is close to that considered by the mechanistic scheme.

Figure 5. Simulated and measured trends in formic acid conversion as a function of formic acid concentration (Case II, Table 1) at 200 °C and 300 °C.

Figure 6 depicts the surface species coverage determined at different formic acid concentrations at 300 °C and 200 °C. Concordant with the previously observed formic acid order change to more negative values when determined at a higher formic acid concentration regime [11], the formate coverage increased with increasing gas phase formic acid concentration. This occurred at the expense of the molecularly adsorbed and activated oxygen species (O_2^* , HOO^* and O^*), which decreased with increasing formic acid concentration. Such a reciprocal relationship between the formates and the activated oxygen species is characteristic of the competitive adsorption of these species. The relatively high coverage of hydroperoxy species at low formic acid concentration is supported by experiments showing lower order in oxygen. The decreased availability of the activated oxygen species causes the lower conversion values at higher gas phase formic acid concentrations (Figure 5). The free sites (*) underwent little change suggesting that a dynamic trade-off results from an increased formate formation and site regeneration upon formate decomposition. The coverage of hydroxyls experienced only a modest decrease owing to competitive reactions contributing to their consumption and production (steps 5 to 8 and 10 to 16, Table 2). Coverage of adsorbed water decreased only marginally suggesting that it is not substantially displaced by formic acid. This is because formate formation (step 7, Table 2) consumes hydroxyls produced from water (steps 5 and 13, Table 2) as well as generates water that can be re-adsorbed on the active site.

Figure 6. Predicted surface coverages as a function of formic acid concentration (Case II, Table 1) at 300 °C (left) and 200 °C (right).

3.2.2. Case III: Varying the oxygen concentration

Figure 7 plots the influence of oxygen on the experimentally and predicted formic acid conversion at 200 °C and 300 °C. Previously, we demonstrated that oxygen is indispensable for carbon dioxide production, without which gold does not catalyze formic acid decomposition [43]. Additionally, the order in oxygen was positive.

Figure 7. Simulated and measured trends in formic acid conversion as a function of oxygen concentration (Case III, Table 1) at 200 °C and 300 °C.

Figure 8. Predicted surface coverages as a function of oxygen concentration (Case III, Table 1) at 300 °C (left) and 200 °C (right).

Though the predicted conversions increased, they lagged behind the experimental values at lower oxygen concentrations (1 and 1.5%). Such a deviation may arise from the intrinsic design of the experimental setup. To avoid pulsations in the water concentration, the experimental setup employed a water dosing system based on the catalytic oxidation of hydrogen by a slight stoichiometric excess of oxygen [41]. Hence, the higher measured conversion values at very low oxygen concentration $\leq 0.02\%$ could be an artefact derived from the presence of a small excess of oxygen compared to the set value. At 200 °C, the observed difference ($\leq 4\%$) can be partly accounted by the contribution of homogenous gas phase formic acid decomposition that occur at low conversions [9].

Figure 8 presents the computed surface coverages as a function of oxygen concentration at 300 °C and 200 °C. An increase in the oxygen concentration increased the oxygen-derived surface species (O_2^* , HCO^* and O^*). The formate coverage remained practically unaffected with changing oxygen coverage. This was experimentally verified by determining the formic acid orders at different oxygen concentrations, which essentially remained constant irrespective of the oxygen concentrations. Such a trend can be explained by taking into account the ‘reservoir-effect’ [53]. The dynamic equilibrium between the adsorbed formates on titania and on the active sites (*) can rapidly replenish the formates as they are increasingly decomposed with rising oxygen concentrations, consequently sustaining constant formate coverage at steady state. High coverage of adsorbed hydrogen may result from direct dehydrogenation of the C-H bond of formates on gold-related active sites (*) at very low surface concentrations of activated oxygen species [18]. With increasing oxygen

concentrations, adsorbed hydrogen are readily captured [18,24,57,58] (step 15, Table 2) leading to a rapid decrease in their coverage.

3.2.3. Case IV: Varying water concentration

Figure 9 depicts the influence of water concentration on the predicted and measured formic acid conversions at 200 °C and 300 °C. The mechanism predicts higher water orders (~ 0.5) than the experimentally determined value (0.1–0.3) [43]. Such a difference can be explained by considering two phenomena. Since water is also a product, ODH of formic acid can be regarded as being autocatalytic. Additionally, the formic acid dehydration reaction taking place independently and simultaneously on titania rises the local water concentrations near the gold-related active sites (*) producing carbon dioxide. Considering that water is not a stoichiometric reactant and only acts as a co-catalyst, very small concentrations should suffice to realize the water-induced promotional effect. In fact, a significant rate enhancement for carbon monoxide oxidation on Au/TiO₂ was realized at ultralow water concentrations between 0.1–3000 ppm [14,59]. Furthermore, the promotional effect of water is proposed to depend on the amount of adsorbed water on the catalyst rather than on the gas-phase water concentration. Hence in our study, it can be hypothesized that the slower response and faster stabilization of the measured formic acid conversion reflects the higher actual water coverage that exceeds the water coverage predicted by the idealistic model at identical gas phase water concentrations.

Figure 9. Simulated and measured trends in formic acid conversion as a function of water concentration (Case IV, Table 1) at 200 °C and 300 °C.

Figure 10 illustrates the trends in the predicted surface coverages derived from increasing water concentration at 300 °C and 200 °C. Reasonably, the surface adsorbed water increased with increasing water concentration. This was accompanied by an increase in the hydroperoxyls and hydroxyls by approximately one order of magnitude. Such an increase is consistent with the findings showing the critical role of water in the generation of the active hydroperoxyls that are critical for formate decomposition in the RDS [53]. Concomitantly, the formate coverage was reduced. Such a decrease can be triggered by two factors: increased consumption owing to increased availability of activated oxygen species and/or displacement of formates by water. In situ DRIFTS of formic acid adsorption under differential feed conditions [43] revealed that, while formates adsorbing on bare titania were prone to non-reactive desorption, the formates on the gold catalyst displayed significantly higher stability. Hence, it can be deduced that the decrease in the formate coverage with increasing water concentration occurs due to the accelerated rate of decomposition to form carbon dioxide.

Figure 10. Predicted surface coverages as a function of water concentration (Case IV, Table 1) at 300 °C (left) and 200 °C (right).

4. Conclusions

In this work, numerical modeling of the proposed ODH mechanism yielded satisfying agreement with the experiments. The inhibiting effect of increasing formate coverage on the catalytic rates was accurately described by the model. On the other hand, adsorbed oxygen and water, which remained well below saturation coverages, promoted the rates by providing the active hydroperoxyls required for formate decomposition in the rate-determining step.

Trends in surface coverages, calculated using the surface perfectly stirred reactor model, were in agreement with kinetic and spectroscopic measurements. The satisfactory convergence between the model predictions and experiments might be further improved by integrating side processes related to carbon monoxide formation and homogeneous gas phase formic acid decomposition to carbon dioxide in the mechanistic scheme.

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Graphical abstract

Comparisons of predicted and measured formic acid conversions as a function of temperature.