Water-Assisted Oxygen Activation during Gold-Catalyzed Formic Acid Decomposition under SCR-Relevant Conditions

Manasa Sridhar^{a,b}, Davide Ferri^a, Jeroen Anton van Bokhoven^{a,b*}, Oliver Kröcher^{a,c*}

^aPaul Scherrer Institut, CH-5232 Villigen, Switzerland

^bETH Zurich, Institute for Chemical and Bioengineering, CH-8093 Zurich, Switzerland

^cÉcole polytechnique fédérale de Lausanne (EPFL), Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland

To be submitted to: Journal of Catalysis

*Corresponding authors:

Oliver Kröcher

Email: oliver.kroecker@psi.ch

Tel.: +41 56 310 2066

Jeroen Anton van Bokhoven

Email: jeroen.vanbokhoven@chem.ethz.ch

Tel.: +41 44 632 5542

Graphical Abstract

Abstract

Owing to the problems associated with the usage of urea as the ammonia precursor compound in the selective catalytic reduction (SCR) process in automobiles, alternative compounds such as ammonium formate, methanamide and guanidinium formate have been suggested as more efficient and cleaner candidates. For the application of such formate-based ammonia precursors, a fundamental understanding of catalytic formic acid decomposition in the presence of the diesel exhaust components water and oxygen is required. Oxygen activation is a reaction step common to many catalytic processes. We observed that oxygen activation over titania and base-modified titania-supported gold catalysts is greatly enhanced in the presence of water, resulting in a significant increase in carbon dioxide production from the decomposition of formic acid. Unlike the supports, gold catalyzed the selective production of carbon dioxide. Monodentate and bidentate formates are the kinetically relevant surface species for carbon monoxide and carbon dioxide production, respectively. The support acts as a reservoir, storing bidentate formates that do not react in the steady state when formic acid and oxygen (and water) are co-fed. However, during transient experiments, when the feed is switched from formic acid to oxygen (and water), they are reactivated upon reverse spillover to the active site associated with gold, where they decompose to carbon dioxide. In the presence of oxygen and water, carbon monoxide oxidation and the water gas shift reaction do not produce carbon dioxide. Instead, a direct oxidative-dehydrogenation-type (ODH) pathway proceeds, which strongly differs from stoichiometric formic acid decomposition. A kinetically consistent mechanism is proposed in which the hydroperoxy species facilitate the C-H bond cleavage of formates to release carbon dioxide and water in the rate-determining step.

Keywords: Formic acid decomposition, gold, water-assisted oxygen activation, hydroperoxy species, kinetic study, DRIFTS

1. Introduction

Selective catalytic reduction (SCR) using urea as the ammonia precursor is widely applied for regulating nitrogen oxide (NO_x) emissions from heavy-duty and light-duty diesel vehicles [1,2]. However, the application of urea is, in practice, impeded by several problems [3,4]. Alternative ammonia precursors, such as concentrated guanidinium formate, ammonium formate (AmFo), and methanamide solutions, have been proposed to replace urea because they are more thermally stable, freeze at lower temperatures, have a higher ammonia storage capacity, and decompose more selectively [4–7]. These precursors undergo thermolysis in the hot exhaust to produce formic acid in the gas phase [3]. Thus, the successful application of these formate-based compounds in the SCR process relies on the development of dedicated catalysts that rapidly decompose formic acid to carbon dioxide in the highly oxidizing exhaust feed (Eq. 1) to prevent formic acid emissions and side product formation from reactions with co-evolved ammonia (Eq. 2 and 3) [3]. Additionally, the catalyst needs to be inert for ammonia oxidation [8].

Scheme 1 compares the possible pathways for carbon dioxide and carbon monoxide formation from formic acid decomposition as reported in literature [9,10] and observed in our studies [8,11,12]. Stoichiometric formic acid decomposition follows two main pathways: dehydration and dehydrogenation, which are selective to carbon monoxide and carbon dioxide, respectively. During formic acid decomposition in the simulated exhaust feed composed of 10 vol% oxygen and 5 vol% water, we demonstrated that gold catalysts predominantly produced carbon dioxide along with low yields of carbon monoxide (Scheme 1) [8,11,12]. Despite the negligible activity for hydrogen oxidation, no hydrogen was detected during formic acid decomposition, suggesting that stoichiometric dehydrogenation did not take place under the investigated conditions. The presence of gas-phase ammonia greatly improved the formic acid decomposition activity and the carbon dioxide selectivity of Au/TiO₂ [12]. The gas-phase promotional effect was realized as a catalytic effect by support modification with a basic additive (lanthana) [11]. Gold supported on lanthanum-modified titania (Au/La-TiO₂) exhibited significantly enhanced rates, and carbon monoxide production was restricted to a lower level (Scheme 1). Such an enhancement was traced back to two

effects, namely, smaller gold particle size (Figure S1) and lanthanum-induced promotion. By thermal aging of the Au/La-TiO₂ catalyst to grow the gold particles to a size range similar to that of Au/TiO₂, we disentangled the two effects and showed that Au/La-TiO₂ retained higher activity compared to Au/TiO₂ even after thermal treatment. Furthermore, carbon dioxide formation via oxidation of carbon monoxide was excluded based on the low activity of Au/TiO₂ and Au/La-TiO₂ for carbon monoxide oxidation (Figure S2) [11]. Hence, a direct pathway is responsible for carbon dioxide production and is associated with the presence of gold.

Formates have been widely proposed as reaction intermediates in mechanisms related to formic acid decomposition [9,10,15] and the water gas shift (WGS) reaction. In the context of fuel cells, several studies investigating stoichiometric formic acid dehydrogenation to hydrogen (and carbon dioxide) have reported formates to be the kinetically relevant surface species and their C-H bond cleavage to be the rate-determining-step [16–21]. The catalytic links between WGS and formic acid decomposition are well-established in the literature, which largely presents a consensus that C-H bond breakage is the rate-determining-step [22–29]. Apart from studies on the promotional effect of water on formate decomposition during WGS, reports on the influence of oxygen and water on the formic acid decomposition chemistry are scarce.

In this work, we examine the origin of the formic acid decomposition activity of 0.5 wt% Au/TiO₂ and 0.5 wt% Au/La-TiO₂ by systematically investigating the consequences of excess oxygen and water (SCR-relevant conditions) on the reaction kinetics and the reactivity of the spectroscopically observed surface species. Using these findings, we propose a mechanism that reconciles the different perspectives prevalent in literature. This work reveals that in the presence of oxygen and water, an oxidative-dehydrogenation type reaction converts formic acid to carbon dioxide and water, which is different from stoichiometric formic acid dehydrogenation to carbon dioxide and hydrogen.

2. Experimental

The preparation and testing of the titania-supported gold catalysts are described elsewhere [8,11,12]. Briefly, anatase titania (DT51, Crystal Global) and anatase titania modified with 10 wt % La₂O₃ (DT57, Crystal Global) were impregnated with a 0.032 M solution of HAuCl₄ (Sigma-Aldrich), calculated on the basis of the volume of water equivalent to the pore volume of the support. The final gold loading was 0.5 wt%. Aging and washing with aqueous

ammonia solution and distilled water, in that order, were followed by calcination at 400 °C for 5 h in air. The unmodified and base-modified catalysts will henceforth be referred to as Au/TiO₂ and Au/La-TiO₂, respectively, and the corresponding supports as titania and La-TiO₂. The HAADF-STEM images of these catalysts are presented in Figure S3 and a more detailed characterization is provided in our previous work [12]. The materials were wash-coated on cordierite monoliths (~2.5 g L⁻¹) and tested in a dedicated setup under spray conditions [30]. The gaseous reaction products at the reactor outlet were quantified by FTIR spectroscopy (Antaris, Thermo Nicolet gas cell) [6]. The total flow rate was set at 750 L h⁻¹, and the contact time was varied by changing the number of monolith pieces stacked along the length of the reactor while keeping constant the total catalyst concentration per unit volume. For experiments to determine the kinetic orders, the concentrations of formic acid, carbon monoxide, oxygen, carbon dioxide, and water were varied in the range 0-2,200 ppm, 0-750 ppm, 0.25-4.00 vol %, 0-750 ppm, and 0.01-1.50 vol%, respectively. External and internal mass transfer limitations were ruled out under the investigated conditions [11]. The formulas 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 carbon monoxide, carbon dioxide and formic acid. Temperature-programmed oxidation and time-on-stream experiments revealed that no carbon deposition occurred on the catalysts.

The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study of formic acid adsorption under steady state and transient conditions was conducted using a Vertex 70 spectrometer (Bruker) equipped with a liquid-nitrogen-cooled MCT detector and a Praying Mantis mirror accessory (Harrick). A customized in situ cell with a flat CaF₂ window was used, designed to perform gas pulses according to the modulation excitation approach frequently used in our group [59,60]. The cell exhibits an exchange rate that is 3.6 times faster compared to the commercial cell (Figure S12). The 95% decay time in the customized cell is 15 s, compared to 54 s for the commercial version. The gas exiting the cell was analyzed in transmission mode using an Alpha spectrometer (Bruker) equipped with a 7 cm gas cell. Prior to each experiment, the sample was pretreated at 400 °C for 0.5 h in a flow of nitrogen containing 10 vol% oxygen and 5 vol% water to remove any carbonate residues present on the catalyst surface. Then, the sample was cooled to 260 °C or 200 °C in flowing nitrogen, at which point the background spectrum was collected. For steady-state experiments, formic acid (1,120 ppm unless otherwise stated) was added to the desired feed gas containing only nitrogen, 10 vol% oxygen, and 5 vol% water or a mixture comprising 10

vol% oxygen and 5 vol% water at a total flow rate of 50 mL min⁻¹, and the adsorption was monitored for 17 min. For the transient experiments, formic acid adsorption in nitrogen was followed by a rapid switch of the feed gas to nitrogen, oxygen, water, or an oxygen-water mixture in nitrogen. All DRIFT spectra were collected by accumulating 100 scans at a resolution of 4 cm⁻¹ and a scanner velocity of 80 kHz.

3. Results

3.1 Effect of oxygen and water on activity

Figure 1 depicts the influence of oxygen and water on the activity of Au/TiO₂ and Au/La-TiO₂ for formic acid decomposition at 200 °C and 300 °C at different contact times. At 300 °C, Au/TiO₂ exhibited the highest decomposition activity in the dry feeds containing oxygen or only nitrogen. The lowest conversion was obtained when only water was added to the formic acid feed. Au/La-TiO₂ exhibited similar behavior, except that the highest conversion was obtained in oxygen and the oxygen-water mixture. At 200 °C, the presence of both oxygen and water was essential to achieve high formic acid conversion on both catalysts. When the feed contained only nitrogen or water, Au/La-TiO₂ exhibited less than 3% conversion, which falls within the range of homogenous (non-catalytic) gas-phase conversion [12]. Au/TiO₂ displayed essentially similar trends irrespective of temperature, except that the decomposition activity was slightly higher and reached ~10% conversion in nitrogen. The WGS activity of the two catalysts was examined in a feed composed of 5 vol% water and 750 ppm carbon monoxide to maintain concentrations equivalent to the formic acid decomposition experiments. The two catalysts exhibited negligible carbon dioxide production under WGS conditions. Additionally, the activity for carbon monoxide oxidation in the presence of water on Au/TiO₂ and Au/La-TiO₂, presented in Figure S2, shows that carbon dioxide production was significantly lower (by 5 times) compared to that arising from formic acid decomposition in oxygen-water mixture. This result confirms that even the contribution of oxygen-assisted WGS is too small to make any significant contribution to the overall carbon dioxide production from formic acid decomposition.

Figure 2 illustrates the influence of the feed composition on the product distribution from formic acid decomposition conducted on Au/TiO₂ and Au/La-TiO₂. The two catalysts exhibited similar feed-dependent behavior. Carbon monoxide was the only other product apart from carbon dioxide. At 300 °C, using the highest contact time, stoichiometric formic acid decomposition in nitrogen led to a 95% yield of carbon monoxide on Au/TiO₂. This

reaction pathway was reduced by a factor of about three by the introduction of water, while the carbon dioxide yield underwent only a modest increase of 2-3%. The latter largely arises from the homogeneous gas-phase formic acid conversion (~3%) [12] and a very small extent of stoichiometric formic acid dehydrogenation [17,31,32]. In oxygen, the carbon dioxide yield was ~35% and further increased to ca. 70% upon the addition of water. At 200 °C, the combined presence of oxygen and water was highly beneficial for formic acid decomposition. The carbon dioxide yield underwent close to three-fold increase on both catalysts upon switching from oxygen to the oxygen-water mixture, whereas carbon monoxide formation was fully suppressed.

Figure 3 compares the formic acid decomposition activity of titania and La-TiO₂ with that of the corresponding gold catalysts. Irrespective of the feed composition, the bare supports produced only carbon monoxide. At 200 °C and 300 °C, the carbon monoxide yields obtained in water and nitrogen on the gold catalysts matched well with those on the corresponding supports. However, at 300 °C, the carbon monoxide yields obtained in oxygen and oxygen-water mixture on the gold catalysts were considerably lower than those on the corresponding supports.

3.2 Reaction orders

The formic acid orders for carbon dioxide production (Table 1) were negative on both catalysts under all conditions. Consistent with the higher surface basicity [11], Au/La-TiO₂ exhibited more negative formic acid orders than Au/TiO₂. The orders became less negative in the regime of lower gas-phase formic acid concentration and higher temperature. This finding, along with the observation of coverage-dependent activation energies [11], is indicative of an underlying compensation phenomenon. In the dry feed, the formic acid orders were slightly less negative. The reaction order for oxygen was ca. 0.3, whereas the water orders were always positive, ranging between 0.1 and 0.3 for both catalysts. Zeroth orders in carbon monoxide and carbon dioxide were observed, indicating the absence of kinetic inhibition by the products.

The formic acid orders for carbon monoxide production (Table 1) in the wet feed varied from slightly negative (-0.1) to more positive values (ca. 0.5) as the gas-phase formic acid concentration was increased. The dry feed resulted in negative formic acid orders in the range of -0.7 to -0.4. The reaction orders in oxygen were always close to zero, whereas those in water were negative (ca. -0.5).

3.3 Effect of feed composition on the apparent activation energy

The apparent activation energy (E_a) and the Arrhenius constant (A) (Table 2) for carbon dioxide production on Au/La-TiO₂ were always higher than those on Au/TiO₂. The presence of water in the feed caused a decrease of E_a from 65 kJ mol⁻¹ to 53 kJ mol⁻¹ and from 42 kJ mol⁻¹ to 34 kJ mol⁻¹ on Au/La-TiO₂ and Au/TiO₂, respectively. The very low carbon dioxide production in the feeds containing only water and only nitrogen (Figure 2) was in the range for homogeneous gas-phase formic acid conversion [12], and thus no E_a was determined. In agreement with the high E_a values (~100 kJ mol⁻¹) reported in literature for formic acid decomposition to carbon monoxide [33,34], both catalysts exhibited an E_a of ~90 kJ mol⁻¹. In water, the E_a for carbon monoxide formation increased by 10-20 kJ mol⁻¹. The presence or absence of oxygen did not affect the E_a .

3.4 In situ DRIFTS study

3.4.1 Formic acid adsorption

Figure 4 depicts the in situ DRIFT spectra obtained after formic acid adsorption at 200 °C and 260 °C in different feeds on the supports [35]. Both supports exhibited strong signals in the region of 1,600-1,300 cm⁻¹, corresponding to the $\nu_{as}(\text{OCO})$ and $\nu_s(\text{OCO})$ stretching modes of the carboxyl groups of adsorbed formates in the bidentate and bridged geometries. Additionally, the signals at 2,954 cm⁻¹, 2,869 cm⁻¹, and 2,731 cm⁻¹ correspond to the combination band $\nu_{as}(\text{OCO}) + \delta(\text{CH})$, the $\nu(\text{CH})$, and the $2\delta(\text{CH})$ overtone, respectively [36]. Various shoulders on both sets of signals indicate multiple adsorption geometries. Monodentate formate species contribute to the bands at ca. 1,680 cm⁻¹ and 1,320 cm⁻¹ on the two supports [37]. No signals corresponding to molecularly adsorbed formic acid species were detected.

The bridged/bidentate formates, with $\nu_{as}(\text{OCO})$ signals at ca. 1,590 cm⁻¹ and 1,560 cm⁻¹ and $\nu_s(\text{OCO})$ signals at ca. 1,380 cm⁻¹ and 1,340 cm⁻¹, remained essentially unaffected on La-TiO₂ upon altering the feed composition. The monodentate formates at 1,690 cm⁻¹ disappeared in the wet feed. This result was accompanied by a considerable decrease of gas-phase carbon monoxide in the online FTIR spectra. Upon co-adsorption of formic acid and water on titania, the overall intensity of the formate signals was lowered along with a suppression of the monodentate formates. Water replenished the hydroxyls that were depleted during formic acid adsorption, as evident from the partial restoration of signals in the 3,800-3,500 cm⁻¹ region. Formic acid adsorption on the supports was not significantly affected by the presence of oxygen.

Figure 5 presents the infrared spectra of the two gold catalysts. Similar to the support counterparts, formates were the dominant surface species during formic acid adsorption in the different feeds. No signals of adsorbed carbon monoxide on gold were observed. The shoulder at approximately $1,635\text{ cm}^{-1}$, in the spectra obtained from the feeds containing water and the oxygen-water mixture, is due to physisorbed water on titania [38]. The broad feature centered at approximately $3,500\text{ cm}^{-1}$ is assigned to the $\nu(\text{OH})$ of hydroxyl groups involved in hydrogen bonding [39,40]. The increase of the baseline below $2,700\text{ cm}^{-1}$, not observed for the bare supports, could be a spectral signature of delocalized shallow-trap and conduction-band electrons [41,42]. In line with its higher basicity, Au/La-TiO₂ exhibited a higher formate coverage compared to that of Au/TiO₂ under all feed conditions. Water exposure nearly eliminated the features corresponding to the monodentate formates, which was again complimented by the absence of carbon monoxide in the online FTIR spectra. In contrast, bridged/bidentate formates were not significantly affected by water on either of the catalysts. The similar slopes for the rise of the formate signals (Figure S13) indicate that the rate of formate formation remained unaffected upon flowing water during formic acid decomposition. On both catalysts, the oxygen-water mixture yielded formate coverages comparable to those obtained with only oxygen, but significantly higher carbon dioxide production was noted in the gas phase.

3.4.2 Transient response under different feed conditions

Figures 6 and 7 show the temporal evolution of the C-H stretching mode of bidentate formates at $2,873\text{ cm}^{-1}$ and the corresponding gas-phase carbon dioxide traces obtained on the gold catalysts during different feed switches at $200\text{ }^{\circ}\text{C}$ and $260\text{ }^{\circ}\text{C}$. On both catalysts, the formate coverage slowly decreased when desorption was performed in a nitrogen feed. The desorption rate was slightly improved upon switching to water. The carbon dioxide production was negligible in both experiments, and the switch to water produced formic acid. In marked contrast, switching from formic acid to oxygen resulted in enhanced removal of the adsorbed formates. In this case, the desorption was of a reactive nature, as revealed by the rise of the carbon dioxide signal in the online FTIR spectra. At the end of these switches, the DRIFT spectra still displayed the presence of unreacted formates (Figure S14). The most rapid removal of formates was observed upon switching to the oxygen-water mixture, which also coincided with the highest carbon dioxide production. The spectra recorded at the end of this switch indicated that essentially all of the surface formates had been consumed (Figure S14).

Figure 8 compares the ratios of the carbon dioxide yields produced from the feeds containing the oxygen-water mixture and oxygen, as obtained from the catalytic measurements ($r_{CO_2,catalytic}$, Eq. S1); the slopes of the consumption of formates ($2,873\text{ cm}^{-1}$) in the oxygen-water mixture and oxygen ($r_{C-H,DRIFTS}$, Eq. S2); and the corresponding carbon dioxide peak areas as measured by online FTIR spectroscopy ($r_{CO_2,FTIR}$, Eq. S3). There was a close match in the estimated ratios obtained from the reactor and the DRIFTS studies. In agreement with the higher carbon dioxide yield on the gold catalysts in the oxygen-water mixture (Figure 2), the ratios of the slopes of formate consumption in the oxygen-water mixture and oxygen were always higher than 1, reaching values close to 3 on both catalysts at 200 °C.

Figure 9 illustrates the temporal evolution of $\nu_{as}(OCO)$ of the bidentate and monodentate formates at $1,558\text{ cm}^{-1}$ and $1,676\text{ cm}^{-1}$, respectively, during equivalent transient experiments on the supports at 260 °C. These bands were chosen to allow differentiation of the mono- and bidentate formates on the supports. In contrast to the gold catalysts, bidentate formates on the supports displayed little reactivity in the presence of nitrogen and oxygen. In the wet feed, the bidentate formates were more easily displaced from the surface of titania than from the more basic surface of La-TiO₂. The monodentate formate intensities declined sharply in nitrogen, followed by a slower decay that was virtually independent of the feed composition on the two supports.

4 Discussion

4.1 Catalytic roles of gold and the support: Parallel pathways for carbon dioxide and carbon monoxide formation

Formic acid can decompose to carbon monoxide and/or carbon dioxide (Scheme 1). The bare supports exclusively catalyzed the dehydration route (Figure 3), whereas the gold catalysts catalyzed both routes (Figure 2 and Figure S3). In the absence of oxygen, the gold catalysts were nearly 100% selective to carbon monoxide. Thus, two parallel reaction pathways were active: dehydration on titania and dehydrogenation associated with gold. The presence of oxygen was essential for the selective decomposition of formic acid to carbon dioxide on the gold catalysts (Figure 2). The negligible activity of the gold catalysts for stoichiometric formic acid dehydrogenation to carbon dioxide in comparison to the activities reported in literature [32] can be attributed to the contact times engaged in this study, which are 4 to 6

orders of magnitude lower. The higher E_a values obtained for carbon monoxide formation than for carbon dioxide production (Table 2) suggest that the latter pathway is more kinetically favored.

4.2 Oxygen and oxygen-water synergy: Nature and reactivity of surface intermediates

The activity of the gold-related sites was dependent on the presence of oxygen and further promoted by the co-presence of water (Figure 2). Because the activities for carbon monoxide oxidation (Figure S2) and the WGS reaction (Figure 1) are virtually irrelevant for carbon dioxide production on the gold catalysts under these conditions, carbon monoxide can be excluded as an intermediate. Oxygen and water are most likely involved in a ‘direct pathway’, which in turn is accelerated in the case of the lanthanum-modified catalyst (Figure 2).

Formates were the only detectable surface species on the catalysts, irrespective of the feed conditions and the presence of gold (Figures 4 and 5). Formic acid adsorption was always accompanied by the consumption of surface hydroxyls, resulting in the formation of surface formates and desorption of water. The addition of water during formic acid adsorption restored the depleted hydroxyls only to some extent. The high coverage of formates prevented further hydroxyl formation [25,43].

On supports free of gold, bidentate formates behaved as spectators, displaying very little reactivity to the change of feed composition (Figures 4 and 9). Monodentate formates were linked to carbon monoxide production. The higher intensities of the monodentate formate signals on titania coincide with its higher carbon monoxide yield as compared to La-TiO₂ (Figure 3). The presence of water suppressed the formation of monodentate formates on both these supports, consequently lowering the carbon monoxide production. Water competes for oxygen vacancies on titania, and these are proposed to be the sites for the formation of monodentate formates upon formic acid adsorption [44,45]. These monodentate formates then undergo C-H bond scission over an adjacent oxygen anion to form carbon monoxide and a surface hydroxyl; condensation of two hydroxyls into water regenerates the surface vacancy [45]. Such a competitive adsorption between water and formic acid correlates well with the highly negative water orders (Table 1) and the increased E_a for carbon monoxide formation in the wet feed (Table 2). The higher degree of suppression at the lower temperature (200 °C) is consistent with more negative water orders. Consistent with the oxygen-independent activity

of the supports (Figure 2, Tables 1, and 2), oxygen did not induce any change in the nature or the reactivity of the formate species.

Gold catalysts exhibited higher formate coverages (Figure 5) than the corresponding supports, suggesting that gold catalyzed the formation of formate species either directly, e.g., at the perimeter of the gold particles, by offering an alternative reaction pathway with a lower activation barrier or indirectly, as a consequence of modifying the oxide surface and/or increasing local reactant coverages by spillover processes [25]. Bridged/bidentate formates were the major surface species under all feed conditions (Figures 5 and S14). The highly negative formic acid orders (Table 1), along with the exclusive observation of formates and the absence of adsorbed carbon monoxide signals in the in situ DRIFT spectra (Figures 5 and S14), indicate that the active sites associated with gold have a higher affinity for formic acid than for carbon monoxide. These findings further support the conclusion that carbon monoxide is not a preferred reaction intermediate during formic acid decomposition to carbon dioxide and thus can be disregarded in mechanistic considerations.

Consistent with the lower carbon monoxide production on the gold catalysts (Figures 2 and 3), a lower density of monodentate formates was present than on the gold-free supports. In contrast to the trend on titania and La-TiO₂, the reactivity of bidentate formates was highly contingent on the feed (Figures 5, 6, 7, and S14). The considerably lower surface formate concentrations in oxygen and the oxygen-water mixture than in nitrogen and water (Figure 5) suggest higher rates of formate consumption to form carbon dioxide [46]. The formate surface concentration in the oxygen-water mixture was similar to that in oxygen, although enhanced carbon dioxide formation was observed. This finding indicates that in the presence of both oxygen and water, more formates were converted to carbon dioxide [47].

Switching the feed from formic acid to an oxygen-water mixture caused the consumption of all formates and the desorption of water and carbon dioxide (Figures 6, 7 and S14). Because all of these formates cannot be accommodated on gold and gold is necessary to selectively produce carbon dioxide, we suggest that the support acts as a reservoir of formates, which, in the presence of oxygen, decompose into carbon dioxide after diffusion to gold [25,48,49]. In the absence of gold, most of these formates remain as inert spectators, whereas a minor fraction (the monodentate formates) slowly decompose to form carbon monoxide (Figure 9).

The relative rates of reactive clean-up of bidentate formates in oxygen and the oxygen-water mixture were well correlated with the relative rates of carbon dioxide production in the

two feeds (Figure 8). This result is consistent with a mechanism in which the bidentate formates represent the relevant reaction intermediates for carbon dioxide formation on both catalysts. Thus, the catalytic and in situ DRIFTS experiments provide complementary evidence of the feed-dependent reaction kinetics and the reactivity of the formate intermediate.

Scheme 2 summarizes these findings. Formates constitute the major surface species on the catalysts and the gold-free supports under all reaction conditions. Monodentate formates are the precursors of carbon monoxide and experience competitive adsorption with water, which in turn lowers the carbon monoxide yield. The bidentate formates react only in the presence of gold and oxygen. The gold catalyst is more densely populated by bidentate formates. The shaded region surrounding the gold particle denotes the area on the support acting as a dynamic sink for the formates, which, in the presence of oxygen, decompose to carbon dioxide on the active sites associated with gold. This pathway is enhanced in the presence of water.

4.3 A hydroperoxyl-mediated mechanism for oxidative dehydrogenation of formic acid: From elementary steps to global kinetics

The carbon dioxide production increased with increasing concentrations of oxygen and water in a manner consistent with Langmuir-Hinshelwood rate equations on surfaces with oxygen- and water-derived species present below saturation coverages. The absence of first-order kinetics in oxygen (Table 1) precludes irreversible oxygen adsorption. Steps 1 and 2 represent the quasi-equilibrated, non-dissociative adsorption steps for oxygen and water on the active site ‘*’.

The water-assisted oxidative decomposition of formic acid to carbon dioxide can be described by the role of water as a co-catalyst, offering an additional, energetically favorable pathway for oxygen activation [50,51]. Such a route for the activation of bimolecular oxygen is similar to the hydroperoxy (HOO^*) route proposed for carbon monoxide oxidation on supported gold catalysts [52–54] and is supported by the water-induced reduction of the E_a (Table 2) of carbon dioxide production. Thus, its formation compensates for the entropic penalty, owing to its larger and more ordered transition state than that for unimolecular

dissociation. Step 3 describes the proton shift equilibrium responsible for the creation of the hydroperoxy species.

Step 4 is the dissociative adsorption of formic acid on the active site, where a surface hydroxyl abstracts the proton to form a formate and a water molecule. In contrast to the positive orders in oxygen and water, the highly negative formic acid order for carbon dioxide production (Table 1) implies that the decomposition mechanism generates high coverages of formates. Therefore, the oxygen-involving step(s) of reactive desorption of these species (e.g., oxidative-dehydrogenation of formate to carbon dioxide) become(s) rate-limiting [55]. The hydroperoxy species that compete for the same adsorption site (step 3) are proposed to cleave the C-H bond of the formate in the rate-determining-step, leading to the release of carbon dioxide and water (Step 5). DFT calculations showed that the α C-H bond of an alcohol can be easily cleaved by hydroperoxy species without involving atomic oxygen during the aerobic alcohol oxidation reaction under aqueous conditions [56]. Direct experimental evidence and the reactivity of such species in the C-H bond activation during propylene epoxidation was established using in situ UV-Vis and electron paramagnetic resonance [57]. In step 6, the atomically adsorbed oxygen species (O^*) resulting from step 5 are removed by reaction with another adsorbed formate (step 6). Carbon dioxide production on both Au/TiO_2 and Au/La-TiO_2 shows highly negative formic acid orders, confirming that the classical effect of basicity, associated with an increased degree of formic acid deprotonation to formate, does not entail higher activity. Hence, lanthanum-modification must accelerate steps 5 and 6, leading to increased carbon dioxide production.

The catalytic cycle is completed by the kinetically irrelevant steps of recombination of the resulting hydroxyls to form water and O^* (step 7), dissociation of adsorbed water into a surface hydroxyl and a proton (step 8), and the reaction of O^* and the surface proton to form surface hydroxyl (steps 9). Because water is regenerated in steps 4 and 5, its role is that of a co-catalyst and not of a stoichiometric reactant. In agreement with our study, Nijhuis and coworkers [58] showed that even though water was not consumed, its presence is critical for the formation of the active hydroperoxy species.

Steps 5 and 6 are the rate-determining-steps of the proposed mechanism. Because O^* is a transient species, i.e., $d[\text{O}^*]/dt = 0$, the pseudo-steady state approximation can be applied for these steps. HCOO^* is considered to be the most dominant surface species, as justified by the formic acid kinetic orders close to -1.

The overall stoichiometric equation is:

The overall reaction rate is the sum of the rates of steps (5) and (6), giving:

$$\text{Rate} = \frac{2(k_5 K_{2\text{eq}} K_{3\text{eq}})^{1/3} (k_6 K_{7\text{eq}})^2 (p_{\text{H}_2\text{O}})^{2/3} (p_{\text{O}_2})^{1/3} L}{(K_{1\text{eq}})^{1/3} K_{4\text{eq}} p_{\text{HCOOH}}}, \text{ where } L \text{ is the total number of sites.}$$

The rate expression derived from the proposed mechanism elicits orders that accurately match the experimentally observed kinetic orders. The full mathematical derivation is provided in the ESI.

The predicted orders for water are higher than the experimentally observed values, which can have two plausible explanations. (i) The dehydration reaction occurring in parallel on the support and forming carbon monoxide and water is expected to increase the local water concentrations, thus lowering the water orders. Complementary to this argument, we observed a more positive water order for carbon dioxide production at 200 °C than at 300 °C (Table 2), which coincided with lower carbon monoxide production. (ii) Considering that the oxidative-dehydrogenation-type (ODH) pathway of formic acid is autocatalytic with respect to water and that the absolute gas-phase water concentrations may be higher than the calculated values arising from the contribution of water present as an impurity in the other reagents (formic acid, oxygen, hydrogen), it is reasonable that the catalytic surface harbors much higher quantities of adsorbed water species with increasing water concentration, thus lowering the apparent water orders. Analogous to our findings, Chandler and coworkers [54] reported that the experimentally determined water orders (~0.3) during water-assisted carbon monoxide oxidation on Au/TiO₂ were lower by a factor of four, as compared to those based on the hydroperoxyl-mediated mechanism (1.3).

5. Conclusions

This work provides mechanistic understanding of formic acid decomposition on titania-supported gold catalysts under conditions relevant to diesel exhaust, thus, marking an important step towards realizing formate-based ammonia precursors as alternatives to urea in the exhaust aftertreatment systems. It was found that gold is catalytically inactive in the absence of oxygen. Carbon monoxide is not a reaction intermediate, and carbon dioxide is produced via a direct oxidative-dehydrogenation-type mechanism. Bidentate formates are the kinetically relevant intermediates to carbon dioxide. Water participates as a co-catalyst, assisting oxygen activation via the formation of the active intermediate (hydroperoxy species) which in turn cleaves the C-H bond of the formate in the rate-determining-step.

Acknowledgments

Financial support from the Swiss National Science Foundation (SNF, project number 200021_143430/1) is gratefully acknowledged.

References

- [1] T.V. Johnson, *Int. J. Engine Res.* 10 (2009) 275–285. doi: 10.1243/14680874JER04009.
- [2] G. Centi, S. Perathoner, in: P. Granger and V.I Pârvulescu (Eds.), *Past and Present in DeNOx Catalysis - From Molecular Modelling to Chemical Engineering*, Elsevier, Amsterdam, 2007, p. 1-23.
- [3] O. Kröcher, M. Elsener, E. Jacob, *Appl. Catal. B Environ.* 88 (2009) 66–82. doi: 10.1016/j.apcatb.2008.09.027.
- [4] M. Eichelbaum, R.J. Farrauto, M.J. Castaldi, *Appl. Catal. B Environ.* 97 (2010) 90–97. doi: 10.1016/j.apcatb.2010.03.027.
- [5] O. Kröcher, P. Daniel, Ammonia generator converting liquid ammonia precursor solutions to gaseous ammonia for denox-applications using selective catalytic reduction of nitrogen oxides, WO 2012104205 A1 (2012). Patent.
- [6] A.M. Bernhard, D. Peitz, M. Elsener, O. Kröcher, *Top. Catal.* 56 (2013) 130–133. doi: 10.1007/s11244-013-9941-4.
- [7] A. Lundström, T. Snelling, P. Morsing, P. Gabrielsson, E. Senar, L. Olsson, *Appl. Catal. B Environ.* 106 (2011) 273–279. doi: 10.1016/j.apcatb.2011.05.010.
- [8] M. Sridhar, D. Peitz, J.A. van Bokhoven, O. Kröcher, *Chem. Commun. (Camb.)* 50 (2014) 6998–7000. doi: 10.1039/c4cc00196f.

- [9] M. Ai, *J. Catal.* 50 (1977) 291–300.
- [10] J.M. Trillo, G. Munuera, J.M. Criado, *Catal. Rev.* 7 (1972) 51–86. doi: 10.1080/01614947208064710.
- [11] M. Sridhar, D. Ferri, M. Elsener, J.A. van Bokhoven, O. Kröcher, *ACS Catal.* 5 (2015) 4772–4782. doi: 10.1021/acscatal.5b01057.
- [12] M. Sridhar, J.A. van Bokhoven, O. Kröcher, *Appl. Catal. A Gen.* 486 (2014) 219–229. doi: 10.1016/j.apcata.2014.08.034.
- [13] Y.-X. Chen, M. Heinen, Z. Jusys, R.J. Behm, *Langmuir* 22 (2006) 10399–10408. doi: 10.1021/la060928q.
- [14] M. Neurock, M. Janik, A. Wieckowski, *Faraday Discuss.* 140 (2008) 363–378. doi: 10.1039/B804591G.
- [15] J. Criado, F. Gonzalez, J.M. Trillo, *J. Catal.* 23 (1971) 11–18. doi: 10.1016/0021-9517(71)90018-2.
- [16] Q.Y. Bi, X.L. Du, Y.M. Liu, Y. Cao, H.Y. He, K.N. Fan, *J. Am. Chem. Soc.* 134 (2012) 8926–8933. doi: 10.1021/ja301696e.
- [17] D.A. Bulushev, S. Beloshapkin, J.R.H. Ross, *Catal. Today* 154 (2010) 7–12. doi: 10.1016/j.cattod.2010.03.050.
- [18] S.K. Hoekman, A. Broch, C. Robbins, R. Purcell, *Int. J. Greenh. Gas Con.* 4 (2010) 44–50. doi: 10.1016/j.ijggc.2009.09.012.
- [19] Y. Huang, X. Zhou, M. Yin, C. Liu, W. Xing, *Chem. Mater.* 22 (2010) 5122–5128. doi: 10.1021/cm101285f.
- [20] T.C. Johnson, D.J. Morris, M. Wills, *Chem. Soc. Rev.* 39 (2010) 81–88. doi: 10.1039/b904495g.
- [21] R.H. Julian, *Chem. Commun.* 48 (2012) 4184–4186.
- [22] A. Ueno, T. Onishi, K. Tamaru, *Trans. Faraday Society* 66 (1970) 756.
- [23] T. Shido, K. Asakura, Y. Iwasawa, *J. Catal.* 122 (1990) 55–67. doi: 10.1016/0021-9517(90)90261-H.
- [24] Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A.U. Nilekar, G. Peng, J.A. Herron, D.C. Bell, H. Saltsburg, M. Mavrikakis, M. Flytzani-Stephanopoulos, *Science* 329 (2010) 1633–1636.
- [25] R. Leppelt, B. Schumacher, V. Plzak, M. Kinne, R. Behm, *J. Catal.* 244 (2006) 137–152. doi: 10.1016/j.jcat.2006.08.020.

- [26] S.D. Senanayake, D. Stacchiola, J. Evans, M. Estrella, L. Barrio, M. Pérez, J. Hrbek, J.A. Rodriguez, *J. Catal.* 271 (2010) 392–400. doi: 10.1016/j.jcat.2010.02.024.
- [27] H.N. Evin, G. Jacobs, J. Ruiz-Martinez, U.M. Graham, A. Dozier, G. Thomas, B.H. Davis, *Catal. Lett.* 122 (2008) 9–19. doi: 10.1007/s10562-007-9352-x.
- [28] G. Jacobs, B.H. Davis, *Int. J. Hydrogen Energ.* 35 (2010) 3522–3536. doi: 10.1016/j.ijhydene.2010.01.055.
- [29] J.M. Pigos, C.J. Brooks, G. Jacobs, B.H. Davis, *Appl. Catal. A Gen.* 319 (2007) 47–57. doi: 10.1016/j.apcata.2006.11.014.
- [30] D. Peitz, A. Bernhard, M. Elsener, O. Kröcher, *Rev Sci Instrum* 82. (2011) 084101. doi: 10.1063/1.3617463. PubMed: 21895255.
- [31] D.A. Outka, R.J. Madix, *Surf. Sci.* 179 (1987) 361–376. doi: 10.1016/0039-6028(87)90063-X.
- [32] M. Ojeda, E. Iglesia, *Angew. Chem. Int. Ed.* 48 (2009) 4800–4803. doi: 10.1002/anie.200805723.
- [33] H. Onishi, T. Aruga, Y. Iwasawa, *J. Catal.* 146 (1994) 557–567. doi: 10.1006/jcat.1994.1094.
- [34] G. Munuera, *J. Catal.* 18 (1970) 19–29. doi: 10.1016/0021-9517(70)90306-4.
- [35] K.L. Miller, C.W. Lee, J.L. Falconer, J.W. Medlin, *J. Catal.* 275 (2010) 294–299. doi: 10.1016/j.jcat.2010.08.011.
- [36] G. Busca, J. Lamotte, J.C. Lavalley, V. Lorenzelli, C. Erba, *J. Am. Chem. Soc.* 109 (1987) 5197–5202. doi: 10.1021/ja00251a025.
- [37] L. Liao, W. Wu, C. Chen, J. Lin, *J. Phys. Chem. B* 105 (2001) 7678–7685. doi: 10.1021/jp003541j.
- [38] M. Kantcheva, M.U. Kucukkal, S. Suzer, *J. Catal.* 190 (2000) 144–156. doi: 10.1006/jcat.1999.2757.
- [39] K. Tanaka, J.M. White, *J. Phys. Chem.* 86 (1982) 3977–3980. doi: 10.1021/j100217a018.
- [40] K. Hadjiivanov, V. Bushev, M. Kantcheva, D. Klissurski, *Langmuir* 10 (1994) 464–471. doi: 10.1021/la00014a021.
- [41] D.A. Panayotov, S.P. Burrows, J.T. Yates, J.R. Morris, *J. Phys. Chem. C* 115 (2011) 22400–22408. doi: 10.1021/jp2065024.
- [42] D.A. Panayotov, J.T. Yates, *J. Phys. Chem. C* 111 (2007) 2959–2964. doi: 10.1021/jp066686k.

- [43] M.S. Ide, R.J. Davis, *Acc. Chem. Res.* 47 (2014) 825–833. doi: 10.1021/ar4001907.
- [44] E.A. Ivanov, G.Y. Popova, Y.A. Chesalov, T.V. Andrushkevich, *J. Mol. Catal. A Chem.* 312. (2009) 92–96. doi: 10.1016/j.molcata.2009.07.022.
- [45] M. Aizawa, Y. Morikawa, Y. Namai, H. Morikawa, Y. Iwasawa, *J. Phys. Chem. B* 109 (2005) 18831–18838. doi: 10.1021/jp0523773.
- [46] J.M. Pigos, C.J. Brooks, G. Jacobs, B.H. Davis, *Appl. Catal. A Gen.* 328 (2007) 14–26. doi: 10.1016/j.apcata.2007.04.001.
- [47] B. Chen, C. Shi, M. Crocker, Y. Wang, A. Zhu, *Appl. Catal. B Environ.* 132–133 (2013) 245–255. doi: 10.1016/j.apcatb.2012.11.028.
- [48] O. Joo, K. Jung, S. Han, S. Uhm, D. Lee, S. Ihm, *Appl. Catal. A Gen.* 135 (1996) 273–286. doi: 10.1016/0926-860X(95)00256-1.
- [49] S.L. Silva, R.M. Lemor, F.M. Leibsle, *Surf. Sci.* 421 (1999) 135–145. doi: 10.1016/S0039-6028(98)00844-9.
- [50] A. Bongiorno, U. Landman, *Phys. Rev. Lett.* 95 (2005) 1–4.
- [51] C.R. Chang, Y.G. Wang, J. Li, *Nano. Res.* 4 (2011) 131–142.
- [52] G.M. Mullen, J. Gong, T. Yan, M. Pan, C.B. Mullins, *Top. Catal.* 56 (2013) 1499–1511. doi: 10.1007/s11244-013-0143-x.
- [53] M. Ojeda, B. Zhan, E. Iglesia, *J. Catal.* 285 (2012) 92–102. doi: 10.1016/j.jcat.2011.09.015.
- [54] J. Saavedra, H.a. Doan, C.J. Pursell, L.C. Grabow, B.D. Chandler, *Science* 80 (2014) 1599–1602.
- [55] G.C. Bond, *Catal. Rev.* 50 (2008) 532–567. doi: 10.1080/01614940802480338.
- [56] C. Shang, Z.-P. Liu, *J. Am. Chem. Soc.* 133 (2011) 9938–9947. doi: 10.1021/ja203468v.
- [57] B. Chowdhury, J.J. Bravo-Suarez, N. Mimura, J. Lu, K.K. Bando, S. Tsubota, M. Haruta, *J. Phys. Chem. B* 110 (2006) 22995–22999. doi: 10.1021/jp066008y.
- [58] D.M. Perez Ferrandez, I. Herguedas Fernandez, M.P.G. Teley, M.H.J.M. de Croon, J.C. Schouten, T.A. Nijhuis, *J. Catal.* 330 (2015) 396–405. doi: 10.1016/j.jcat.2015.07.024.
- [59] O. Martin, C. Mondelli, A. Cervellino, D. Ferri, D. Curulla-Ferré, J. Pérez-Ramírez, *Angew. Chemie* 128 (2016) 11197–11202.
- [60] A. Marberger, D. Ferri, M. Elsener, O. Kröcher, *Angew. Chemie Int. Ed.* 55 (2016) 11989–11994.

Figure 1 Formic acid conversion on Au/TiO₂ and Au/La-TiO₂ at 200 °C and 300 °C as a function of contact time (W/F , g s cm⁻³) and feed composition. The WGS activity ($\blacktriangle$) of the two catalysts was determined using equivalent concentrations of carbon monoxide (750 ppm) and 5 vol% H₂O at $W/F = 2.4 \times 10^{-5}$ g s cm⁻³.

Figure 2 Comparison of carbon dioxide and carbon monoxide yields obtained from the decomposition of 750 ppm formic acid over Au/TiO_2 and $Au/La-TiO_2$, using different feed compositions at 200 °C and 300 °C, and $W/F = 2.4 \times 10^{-5} \text{ g s cm}^{-3}$ (left column) and $1.6 \times 10^{-4} \text{ g s cm}^{-3}$ (right column).

Figure 3 Comparison of carbon monoxide yields obtained from the decomposition of 750 ppm formic acid over titania, La-TiO_2 and the corresponding gold catalysts at 200 °C and 300 °C, using different feed compositions: nitrogen (▽), 10 vol % oxygen (○), 5 vol % water (△) and mixture of 10 vol % oxygen and 5 vol % water (□) at $W/F = 1.6 \times 10^{-4} \text{ g s cm}^{-3}$.

Figure 4 DRIFT spectra of formic acid adsorption on titania and La-TiO_2 , obtained under different feed conditions at 200 °C and 260 °C.

Figure 5. Steady-state DRIFT spectra of formic acid adsorption on Au/TiO₂ and Au/La-TiO₂, obtained under different feed conditions at 200 °C and 260 °C.

Figure 6. Temporal evolution of the C-H vibrational mode of formate at 2,873 cm⁻¹ on Au/La-TiO₂ at (a) 200 °C and (b) 260 °C during formic acid adsorption in the indicated feed. (c, d) Corresponding carbon dioxide evolution from gas-phase FTIR analysis.

Figure 7. Temporal evolution of the C-H stretching vibrational mode of formate at 2,873 cm⁻¹ on Au/TiO₂ at (a) 200 °C and (b) 260 °C during formic acid adsorption in the indicated feed. (c, d) Corresponding carbon dioxide evolution from gas-phase FTIR analysis.

Figure 8. Relative yields of carbon dioxide produced from formic acid decomposition on Au/TiO₂ and Au/La-TiO₂ in an oxygen-water mixture and only oxygen. (Δ) Catalytic experiments; ($\square$) ratio between the slopes of the decrease in the C-H signal (2,873 cm⁻¹, transient DRIFTS); ($\circ$) ratio of carbon dioxide peak areas obtained from formic acid decomposition in an oxygen-water mixture to that in only oxygen, derived from gas-phase FTIR analysis.

Figure 9. Temporal evolution of the $-(OCO)-$ stretch signals at $1,558\text{ cm}^{-1}$ and $1,676\text{ cm}^{-1}$ on (a) titania and (b) La-TiO_2 , during formic acid adsorption in nitrogen and sequential desorption in feed containing only nitrogen, water, oxygen, and an oxygen-water mixture at $260\text{ }^\circ\text{C}$.

Scheme 1. Pathways for carbon dioxide and carbon monoxide formation from formic acid decomposition under stoichiometric conditions and in the presence of oxygen and water (SCR conditions).

Scheme 2. Illustration of the surface species and their reactivity under different feed conditions over the support and the catalyst.

Table 1. Reaction orders in formic acid, oxygen, and water for carbon dioxide and carbon monoxide production over Au/TiO₂ and Au/La-TiO₂

Feed condition	Catalyst	Temperature (°C)	CO ₂ production				CO production			
			HCOOH (±0.05)	O ₂ (±0.05)	H ₂ O (±0.1)	CO ₂ /CO (±0.05)	HCOOH (±0.05)	O ₂ (±0.05)	H ₂ O (±0.05)	CO ₂ /CO (±0.05)
Wet	Au/TiO ₂	300	-0.59	0.26	0.17	0.00	-0.15,0.54 ^a	-0.09	-0.34	0.00
		200	-0.72	0.31	0.25	0.00	n.a.	n.a.	-0.64	0.00
	Au/La-TiO ₂	300	-0.74, -0.44 ^a	0.32	0.11	0.00	-0.16,0.52 ^a	-0.08	-0.41	0.00
		200	-0.95, -0.73 ^a	0.31	0.21	0.00	n.a.	n.a.	-0.62	0.00
Dry	Au/TiO ₂	300	-0.49	0.30	-	0.00	-0.38	-0.05	-	0.00
		200	-0.61	0.24	-	0.00	-0.60	-0.04	-	0.00
	Au/La-TiO ₂	300	-0.65	0.36	-	0.00	-0.31	-0.05	-	0.00
		200	-0.75	0.24	-	0.00	-0.69	-0.01	-	0.00

^aDetermined using formic acid concentrations in the range 40-150 ppm in 20 ppm increments.

All values were determined using $W/F = 2.4 \times 10^{-5} \text{ g s cm}^{-3}$ and a total flow of 750 L h^{-1} . The formic acid, carbon monoxide, oxygen, carbon dioxide, and water concentrations were varied in the ranges of 0-2,200 ppm, 0-750 ppm, 0.25-4.00 vol %, 0-750 ppm, and 0.1-1.50 vol%, respectively. The plots used to determine kinetic orders are presented in Figures S4-10.

Table 2. Apparent activation energies (E_a) and Arrhenius constants (A, in parentheses) determined for carbon dioxide and carbon monoxide production from formic acid decomposition on Au/TiO₂ and Au/La-TiO₂ under different feed conditions.^a

Feed composition	Au/La-TiO ₂		Au/TiO ₂	
	CO ₂ production	CO production	CO ₂ production	CO production
O ₂ +H ₂ O	53 (E+10)	89 (E+11)	34 (E+07)	90(E+12)
O ₂	65 (E+10)	76 (E+11)	42 (E+07)	80 (E+11)
H ₂ O	-	103 (E+12)	-	102 (E+12)
N ₂	-	79 (E+11)	-	83 (E+12)

^aAll values were determined using 750 ppm formic acid at $W/F = 2.4 \times 10^{-5} \text{ g s cm}^{-3}$ and a total flow of 750 L h⁻¹. The corresponding Arrhenius plots and the conversion values used to determine E_a and A are presented in Figure S11 and Tables S1-S4, respectively.