Journal of Catalysis 290 (2012) 193-201

Contents lists available at SciVerse ScienceDirect

# Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

# Reaction kinetics studies of the conversions of formic acid and butyl formate over carbon-supported palladium in the liquid phase

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#### ARTICLE INFO

Article history: Received 9 January 2012 Revised 5 March 2012 Accepted 18 March 2012 Available online 20 April 2012

Keywords: Formic acid Formate ester Decarboxylation Decarbonylation Kinetic model H<sub>2</sub> production Pd/C

#### ABSTRACT

Formic acid and butyl formate conversion were studied in the liquid phase over Pd and Ru catalysts. Pd/C was more active, selective, and stable for  $CO_2/H_2$  production in the liquid phase. Kinetic studies were performed over Pd/C at temperatures from 403 to 443 K, at space velocities from 3.8 to 970 h<sup>-1</sup>, in the presence of CO and H<sub>2</sub> at partial pressures from 0 to 0.4 and 12.6 atm, respectively, and liquid water. Space velocity studies probed the importance of primary decomposition pathways to  $CO_2$  and CO compared to the secondary water–gas shift reaction. Generally, the rate of the primary pathway was an order of magnitude higher than the rate of the secondary pathway. Over Pd/C, formic acid decomposed primarily via decarboxylation (to  $CO_2/H_2$ ), whereas butyl formate primarily decomposed via decarbonylation (to  $CO_2$  butanol). When water was present, the formate ester hydrolyzed, which increased the selectivity toward  $CO_2$  and  $H_2$ .

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## 1. Introduction

The need to develop sustainable sources of energy and the potential to use biomass to supplant petroleum are critical to ensure environmental conservation, stimulate economic development, and promote national security. A major challenge to achieve the transition from petroleum-based feedstocks to the use of biorenewable resources is the effective deoxygenation of bio-molecules. To this end, reactions of carboxylic acids and esters have been identified as important reactions for the conversion of biomass feedstocks to hydrogen, fuel grade alkanes, and chemicals [1–5]. The deoxygenation of carboxylic acids and esters can take place by parallel pathways involving dehydrogenation/decarboxylation or dehydration/decarbonylation, as depicted in Scheme 1. Consequently, a fundamental understanding of these reactions for carboxylic acids and esters is necessary to design highly selective processes that efficiently produce fuels and chemicals from biomass.

As the simplest carboxylic acid, formic acid has played a critical role in the elucidation of carboxylic acid reactivity [6]. Formic acid has been utilized as a probe molecule for heterogeneous reactions on metals [7–25], metal-oxides [23,24,26–30], metal carbides [31–33], and oxide-supported metals [34,35]. Researchers employing theoretical and computational methods have also investigated formic acid as a molecule to probe reactivity [36,37]. In general, the

\* Corresponding author. *E-mail address:* dumesic@engr.wisc.edu (J.A. Dumesic). literature exploring the decomposition kinetics of formic acid has focused on homogenous catalytic systems [38–43], surface science studies under ultra-high vacuum (UHV), and gas-phase reactions over heterogeneous catalysts. However, the literature is limited with regard to the decomposition of esters and a direct comparison of how they differ from their associated carboxylic acid [44,45]. Moreover, the parallel pathways in Scheme 1 are connected by the water–gas shift (WGS) reaction [11–14,31,32,34,46], and this connection is especially important in biomass conversion processes that often are carried out in the liquid phase in the presence of water [2,47,48].

Another motivation for studying the decomposition of formic acid is that formic acid is produced as a coproduct during the conversion of cellulose to levulinic acid. Thus, formic acid can be used as a source of H<sub>2</sub> for the reduction of levulinic acid to gamma-valerolactone (GVL), allowing GVL to be produced from biomass without the need for an external source of hydrogen [5]. However, the use of mineral acids to produce levulinic acid and formic acid from cellulose deconstruction has posed significant challenges for downstream upgrading. An interesting strategy to remove the formic and levulinic acids from the acidic aqueous environment is to employ reactive extraction via esterification by reaction with an alcohol or an alkene [4]. Accordingly, the present work was undertaken to explore the reactivity of formic acid and butyl formate as probe molecules over two metal catalysts used in previous work, that is Pd/C and Ru/C. Studies at different space velocities were carried out to elucidate the triangular reaction scheme represented in



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**Scheme 1.** Triangle reaction scheme for the decomposition of formic acid and formate esters. *R* symbolizes either atomic hydrogen or an alkyl group.

Scheme 1, as well as to probe the effects of water on the hydrolysis of the ester in solution. The results of these reaction kinetics studies allow for the evaluation of the individual kinetic contributions of the primary decomposition pathways, secondary WGS reaction, and homogeneous chemistry in solution. Finally, a simple kinetic model is presented to describe the competing reaction pathways and the observed reaction kinetics.

#### 2. Experimental

Reaction kinetics measurements were carried out using a halfinch stainless steel tube as a flow reactor, followed by a gas liquid separator at room temperature. A fixed-bed, down-flow configuration was maintained by using a quartz wool plug at the bottom. The two catalysts studied were purchased from Sigma–Aldrich and consisted of either 5 wt.% Ru or 10 wt.% Pd supported on carbon. The catalyst bed was diluted with crushed, fused SiO<sub>2</sub> (4– 16 mesh, Sigma–Aldrich) in a 1:1 volumetric ratio. The reactor was filled to the top of the heating zone with more crushed, fused SiO<sub>2</sub>. The reactor was heated via aluminum blocks in a well-insulated furnace (Applied Test Systems). The temperature was measured by type-K thermocouples (Omega) and controlled by a PID controller (Love Controls Series 16A) connected to a variable transformer (Staco Energy Products).

Prior to reaction kinetics studies, the catalysts were reduced in situ at 673 K (0.45 K min<sup>-1</sup> ramp) for 2 h. All reaction kinetics measurements were carried out at a temperature of 423 K, unless otherwise noted. Helium and H<sub>2</sub> (Airgas, industrial grade) were co-fed for the space velocity studies, and mixtures of 1% CO in helium and 7% H<sub>2</sub> in helium (Airgas) were co-fed with additional helium for the reaction order studies. The flow rates of gasses were controlled using mass flow controllers (Brooks 5850E), and the total gas flow rate out of the system was measured using a bubble meter. The liquid reagents (formic acid, Sigma-Aldrich, 98-100%; 1-butanol, Sigma-Aldrich, 99.9%; n-butyl formate, Alfa-Aesar, 97%) were used as purchased, and they were fed to the reactor from a graduated cylinder via a needle by a high-performance liquid chromatography (HPLC) pump (Lab Alliance Series I). The total pressure in the reactor was controlled by a back-pressure regulator (GO model BP-60) and maintained at 530 psi.

The adsorption uptake of CO was measured on each catalyst at 308 K using an ASAP 2020 (Mircomeritics) after reduction of the catalyst at 673 K ( $0.45 \text{ K} \text{min}^{-1}$ ) for 2 h. The number of catalytic sites was taken to be equal to the irreversible CO uptake at this temperature.

Experiments were carried out to assess the hydrolysis rate of butyl formate in a batch reactor at 530 psi in a 50 mL stainless steel pressure vessel (Parr Instruments). The reactor was heated using heating tape, and the temperature was maintained at 423 K with the same equipment, reagents, and gases used in the flow reactor experiments. Reaction solutions were delivered by an HPLC pump after heating the pressure vessel to the reaction temperature. Liquid samples were taken via a sampling port and quenched in an ice water bath before analysis.

For all experiments, gas analysis was carried out utilizing a Shimadzu 2014 gas chromatograph with a HaySep DB 100/120 column (Alltech) and a thermal conductivity detector to detect CO and CO<sub>2</sub>. An Agilent GC6890 equipped with an Rtx column (Agilent) and a flame ionization detector was used to detect gas-phase alkanes. Liquid analysis was done by HPLC (Waters 2695 system with either a Bio-Rad Aminex HPX-87H column and a RI 410 detector or an Agilent Zorbax SB-C18 column and a UV detector). Liquid and gas analyses were performed throughout the duration of the experiment. Steady state was usually achieved in less than 8 h over Pd/ C and was not achieved over Ru/C. The system was determined to be free of mass transfer limitations by the Weisz-Prater criterion.

#### 3. Results and discussion

#### 3.1. Catalyst comparison

Figs. 1 and 2 compare the rates and selectivities of formic acid and butyl formate decomposition over Pd/C and Ru/C catalysts. To calculate the turnover frequency (TOF), the rate was normalized by the number of surface sites as measured by the irreversible uptake of CO at 308 K, equal to 126  $\mu$ mol g<sup>-1</sup> for Ru/C (26% dispersion) and 56–110  $\mu$ mol g<sup>-1</sup> for Pd/C, depending on the manufacturer batch number (6–12% dispersion). It can be seen in Figs. 1 and 2 that Pd/C exhibits a higher initial TOF for the decomposition of formic acid and butyl formate compared to Ru/C



**Fig. 1.** TOF (**■**) and CO<sub>2</sub> selectivity (**□**) for decomposition of 2 M formic acid in H<sub>2</sub>O over Pd/C, compared to TOF (**●**) and CO<sub>2</sub> selectivity (**○**) over Ru/C at 423 K, with a He co-feed at 530 psi, and WHSV = 97 h<sup>-1</sup>.



**Fig. 2.** TOF (**■**) and CO<sub>2</sub> selectivity ( $\square$ ) for decomposition of 2 M butyl formate in 1butanol over Pd/C, compared to TOF (**●**) and CO<sub>2</sub> selectivity ( $\bigcirc$ ) over Ru/C at 443 K, with a He co-feed at 530 psi, and WHSV = 30 h<sup>-1</sup>.

 $(0.075 \text{ s}^{-1} \text{ versus } 0.021 \text{ s}^{-1} \text{ for formic acid, and } 0.0047 \text{ s}^{-1} \text{ versus } 0.0045 \text{ s}^{-1}$  for butyl formate), which is in relative agreement for the two catalysts with recent studies by Solymosi et al. [25] for formic acid in the vapor phase. Additionally, Pd/C has a higher selectivity toward the decarboxylation/dehydrogenation pathway than Ru/C (97% versus 90% for formic acid and 48% versus 23% for butyl formate).

The results in Figs. 1 and 2 demonstrate that the rate and  $H_2/CO_2$ selectivity of formic acid decomposition are higher than for butyl formate over both Pd/C and Ru/C. In addition, the Pd/C catalyst exhibits superior stability compared to the Ru/C catalyst. It is probable that the deactivation of the Ru/C catalyst is caused by coking of the catalyst surface, as suggested by the observation of significant amounts of CH<sub>4</sub> production. Since CH<sub>4</sub> production requires the cleavage of CO bonds and the formation of surface C species, it is possible that carbonaceous species accumulate on the surface of the catalyst and block active sites. Support for this hypothesis is provided by the work and literature review of Mukkavilli et al. [49]. Furthermore, CH<sub>4</sub> production is not observed at these conditions over the Pd/C catalyst, consistent with the observation that this catalyst is stable at the reaction conditions of the present study. Accordingly, the Pd/C catalyst is the focus of the further kinetic studies due to its higher activity, selectivity, and stability.

#### 3.2. Primary pathway for formic acid decomposition

The results of this study show that the decarboxylation/dehydrogenation pathway appears to be favored for the decomposition of formic acid in the liquid phase over Pd/C. However, it was not clear whether this high selectivity to CO<sub>2</sub> was due to the primary decarboxylation/dehydrogenation pathway or to the secondary WGS reaction pathway. Accordingly, studies were performed to measure the CO<sub>2</sub>:CO ratio in the product stream at varying weight hourly space velocities (WHSV), starting with a feed of 2 M formic acid in water. At high space velocity, it can be assumed that the contributions of secondary reaction pathways were minimized. The trend illustrated in Fig. 3 can be extrapolated to infinite space velocity to predict a CO<sub>2</sub>:CO ratio of 35:1, which is equal to the rate of dehydrogenation/decarboxylation divided by the rate of dehydration/decarbonylation. This ratio of 35:1 corresponds to a CO<sub>2</sub> selectivity greater than 97%, showing that the high CO<sub>2</sub> selectivities for Pd/C are predominantly due to the dehydrogenation/decarboxylation primary decomposition pathway. Fig. 3 shows that at lower space velocities, the CO<sub>2</sub>:CO ratio can be increased by more than one order of magnitude to greater than 430:1 by allowing the WGS reaction to occur. This order of magnitude increase in the CO<sub>2</sub>:CO ratio corresponds to an improvement in selectivity up to 99.8%. Operating at even lower space velocities would allow WGS to reach equilibrium and could further increase the CO<sub>2</sub>:CO ratio to 1800:1 (99.9% CO2 selectivity).



**Fig. 4.** CO<sub>2</sub>:CO ratio with respect to inverse WHSV for decomposition of 2 M formic acid in liquid water at 423 K and 530 psi with 35% H<sub>2</sub> in He co-feed.

The effect of hydrogen on the decomposition pathway was investigated because decomposition of formic acid is a potential route for production of hydrogen and because many biomass processing strategies involve reactions under hydrogen atmospheres. Fig. 4 illustrates the effect of changing the gaseous co-feed from helium to a mixture of 35% H<sub>2</sub> in helium. The increase in the CO<sub>2</sub>:CO ratio at lower space velocity that is seen in Fig. 3 is largely absent after the addition of H<sub>2</sub> because the predicted WGS equilibrium ratio of CO<sub>2</sub>:CO has shifted to 54:1 in the presence of H<sub>2</sub>. Extrapolating to infinite space velocity using only the data in the region before WGS equilibrium is reached (1/WHSV = 0.0055 h) gives a ratio of CO<sub>2</sub>:CO of 42:1 (97.7% selectivity), similar to the value of 35:1 (97.2% selectivity) obtained in the absence of H<sub>2</sub>.

#### 3.3. Primary pathway for butyl formate decomposition

To gain insight into the selectivity differences between the decompositions of formic acid and butyl formate demonstrated in Figs. 1 and 2, studies were carried out at different space velocities for the decomposition of butyl formate, analogous to those studies carried out for formic acid. Comparison of the results in Fig. 5 for butyl formate with the behavior in Fig. 3 for formic acid demonstrates that changing the functional group from a carboxylic acid to an ester decreases the CO<sub>2</sub>:CO ratio at infinite space velocity due to a change in the primary decomposition pathway. The sharp increase in CO<sub>2</sub>:CO ratio at high space velocity is attributed to the decomposition of a formic acid impurity (up to 3 wt.% of pure buty) formate) in the feed that reacts at a much higher rate than butyl formate, as shown in Figs. 1 and 2. Thus, the CO<sub>2</sub>:CO ratio at lower space velocities (1:10, 8.5%) selectivity to  $CO_2$  is a better indication of the ratio of CO<sub>2</sub>:CO due to the primary pathways of formate ester decomposition. At these higher conversions, the effect of the small impurity of formic acid is mitigated by the higher conversion



Fig. 3. CO<sub>2</sub>:CO ratio with respect to inverse WHSV for decomposition of 2 M formic acid in liquid water at 423 K and 530 psi with He co-feed.



**Fig. 5.** CO<sub>2</sub>:CO ratio with respect to inverse WHSV for decomposition of 2 M butyl formate in 1-butanol at 423 K and 530 psi with He co-feed.



Fig. 6.  $CO_2$ :CO ratio with respect to inverse WHSV for decomposition of 2 M butyl formate in 1-butanol at 423 K and 530 psi with 35%  $H_2$  in He co-feed.

of butyl formate, and the reaction conditions (absence of water or  $H_2$ ) effectively eliminate the secondary WGS reactions (in both the forward and reverse directions).

To explicitly account for the role of H<sub>2</sub> in the decomposition of butyl formate, the gaseous co-feed was switched from He to 35% H<sub>2</sub> in He. As demonstrated in Fig. 6, the presence of H<sub>2</sub> shifted the predicted equilibrium ratio of CO<sub>2</sub>:CO toward CO due to the reverse WGS reaction, while simultaneously shifting the CO<sub>2</sub>:CO ratio at infinite space velocity toward CO<sub>2</sub> (from 1:2 to 4:1). The latter effect is caused by a decrease in the rate of butyl formate decomposition upon addition of H<sub>2</sub>, which thus increases the relative contribution to the rate by decomposition of the formic acid impurity at a given space velocity. It should be noted that the behavior at low space velocities in Fig. 6 is different from that seen in Fig. 4, with the ratio of CO<sub>2</sub>:CO decreasing at low space velocity rather than increasing. This behavior is due in part to a lack of water, which moves the reaction into the reverse WGS regime, and in part to the depletion of the formic acid impurity, which leads to a decrease in the relative contribution of formic acid compared to butyl formate. The CO<sub>2</sub>:CO ratio was equal to 1:4 at low space velocities, with a predicted equilibrium CO<sub>2</sub>:CO ratio of 1:15 due to reverse water-gas shift.

#### 3.4. Effect of water on butyl formate decomposition

In a previous study by Gürbüz et al. [4], it was observed that the addition of water during the decomposition of butyl formate over Pd/C increased both the rate of decomposition and the selectivity toward the decarboxylation pathway. The effect of water concentration on the rate and selectivity of butyl formate decomposition was thus further investigated, and the results of these experiments are shown in Fig. 7, where the concentration of water was varied from 0 to its solubility limit of 6 M in the butyl formate/1-butanol reaction mixture. The addition of 2 M water improved the rate by more than a factor of 2. Further increasing the water concentration to 6 M gave a smaller additional increase in the rate of the reaction. Fig. 7 also shows that the selectivity improvement from the addition of water matches the improvement predicted by assuming all of the increased activity can be attributed to the decomposition of formic acid formed from hydrolysis of butyl formate.

The possible role of hydrolysis contributing to the reactivity of butyl formate was investigated by measuring the rate of hydrolysis in a batch reactor in the absence of the Pd/C catalyst. The hydrolysis reaction was observed to be autocatalytic, because of acid-catalyzed processes enhanced by the formation of formic acid. This behavior suggests that the hydrolysis reaction can occur in the heated zone of the flow reactor even before reaching the catalyst bed. Table 1 shows the calculated equilibrium conversion and the maximum observed rate for autocatalytic hydrolysis of butyl formate at the three different water concentrations. The fastest rate of hydrolysis was lower than the observed rate of formic acid



**Fig. 7.** TOF (**■**) and CO<sub>2</sub> selectivity ( $\bigcirc$ ) for the decomposition of 2 M butyl formate in 1-butanol as a function of water concentration with a co-feed of 35% H<sub>2</sub> in He at 423 K, 530 psi, and a WHSV = 15 h<sup>-1</sup>. The predicted CO<sub>2</sub> selectivity ( $\diamondsuit$ ) is calculated assuming that the increase in rate is entirely due to the decomposition of formic acid formed from the hydrolysis of butyl formate.

Table 1

Thermal hydrolysis of 2 M butyl formate in 1-butanol at 423 K under a pressure of 530 psi as a function of water concentration. The maximum rate and equilibrium conversion are calculated as averages of the rate or extent of generation of formic acid and the rate or extent of consumption of butyl formate.

Water concentration (M)	Maximum rate (µmol min <sup>-1</sup> mL <sup>-1</sup> )	Equilibrium conversion (%)	Predicted equilibrium conversion (%)
2	4.3	4	4
4	7.6	10	9
6	15.7	12	15

decomposition, indicating that all of the formic acid produced during hydrolysis should be consumed as the solution passed over the catalyst bed. This is in agreement with the observation that formic acid was never detected as a product. While the amount of formic acid that was produced in the feed before the catalyst bed is not sufficient to explain the entire increase in rate produced by the addition of water, the hydrolysis reaction likely continued to occur over the catalyst bed. In addition, the hydrolysis of alkyl esters is expected to take place on the catalyst surface, as reported in the heterogeneous catalysis literature [50].

Studies of the decomposition of butyl formate were carried out at different space velocities to probe the effect that the addition of water has on the primary decomposition pathway. The CO<sub>2</sub>:CO ratio increased at higher concentrations of water across the range of space velocities, as shown in Fig. 8. In addition, Fig. 8 shows that the CO<sub>2</sub>:CO ratio extrapolated to infinite space velocity for butyl formate decomposition increased significantly for all water concentrations compared to Figs. 5 and 6 in the absence of water. Importantly, the value of the CO<sub>2</sub>:CO ratio for butyl formate in the presence of water approached that of formic acid decomposition. At the highest space velocity, the selectivity to CO<sub>2</sub> for decomposition of butyl formate with 6 M water nearly equaled that of pure formic acid (95.5% versus 97.7%) and was much higher than the selectivity for butyl formate decomposition without water at high space velocity (95.5% versus 79%). This comparison indicates that hydrolysis of the ester and the subsequent decomposition of the formic acid is the primary cause of the increase in selectivity when co-feeding water.

The addition of water increased the value of the CO<sub>2</sub>:CO ratio that is predicted by the WGS equilibrium (up to 200:1 for the case of 6 M water). Despite this prediction, the observed ratio of CO<sub>2</sub>:CO decreased at low space velocity to a value less than 4:1 for all water concentrations. This behavior indicates that WGS is not the dominant factor in determining the change in selectivity with



**Fig. 8.** CO<sub>2</sub>:CO ratio with respect to inverse WHSV for decomposition of 2 M butyl formate with 2 M ( $\blacksquare$ ), 4 M ( $\bullet$ ), and 6 M ( $\blacklozenge$ ) H<sub>2</sub>O in 1-butanol with 35% H<sub>2</sub> in He co-feed at 423 K, and 530 psig.

decreasing space velocity for the decomposition of butyl formate in the presence of water, but rather the trend in the  $CO_2$ :CO ratio is caused by the interplay between ester hydrolysis and ester decarbonylation. More specifically, at high space velocity, the selectivity is dominated by the decomposition of formic acid formed from butyl formate hydrolysis in the presence of water. At low space velocities, the formic acid has been completely consumed, and the trend in overall selectivity is dominated by the decomposition of butyl formate that has a significantly lower primary pathway selectivity toward  $CO_2$  (observed to be as low as 8.5% experimentally).

We note that the  $CO_2$  selectivity in this paper differs from the value of 100% reported previously because the decomposition of butyl ester in the present study was performed in excess 1-butanol rather than with excess water and formic acid in the co-feed [4]. Thus, the equilibrium conversion and the rate for ester hydrolysis were lower in the present work compared to the previous study. Since the ratio of water to butyl formate was much higher in the previous study, it allowed for more extensive hydrolysis of the ester, thus allowing the overall reaction to proceed almost entirely through formic acid. Additionally, since very low space velocities were used to ensure full conversion in the previous study, there was ample time for WGS to further increase selectivity toward  $CO_2$ , similar to the results observed at low space velocity for formic acid decomposition in the present work.

#### 3.5. Reaction order studies and kinetic modeling

To help describe and quantify the reaction kinetics observed experimentally in this study, a simple kinetic model was developed and implemented in MATLAB by solving the material balance equations for a plug flow reactor (PFR). The complex nature of these reactions with multiple pathways taking place in the liquid phase makes it difficult to extrapolate model parameters from the literature and necessitates the use of a simplified model with a limited number of parameters. This type of simplified model is based on mechanistic reasoning, but does not attempt to explain all the intricacies of the underlying mechanisms of formic acid (FA) or butyl formate (BF) decomposition. Rather the model is used to describe the competing reaction pathways and observed kinetics under the current set of reaction conditions.

Rate expressions based upon the partial pressures of reactants and products were developed by assuming that the compositions of the liquid and gas phases were quasi-equilibrated. The rates of adsorption and desorption from the catalyst surface of all species were assumed to be quasi-equilibrated, the decomposition of formic acid was assumed to be irreversible, and the water–gas shift reaction was assumed to be reversible. Studies of the formic acid decomposition rate at various partial pressures of CO and H<sub>2</sub> (Fig. 9a and b) demonstrated that CO, and to a lesser extent H<sub>2</sub>,



**Fig. 9.** TOF for the decomposition of FA versus partial pressures of (a)  $H_2$ , (b) CO, and (c) FA. Experimental data are given by solid symbols: TOF for decarboxylation/dehydration ( $\blacksquare$ ) and TOF for decarboxylation/dehydrogenation (●). Solid lines show predictions of the kinetic model. Values of X are reaction orders calculated from experimental data.

had detrimental effects on the rate, and thus these species were included in a site blocking term. The low order of  $H_2$  suggested that the surface coverage by H-atoms was only significant at high partial pressures. The rate was inhibited strongly by CO even at low partial pressures, indicating a strong interaction of CO with the catalyst surface. Because the binding of CO with a metal surface is known to be highly dependent on the surface coverage, Eq. (6) was introduced to modify the free energy of CO adsorption as a function of CO partial pressure, similar to the strategy employed by Grabow et al. [51]. The data in Fig. 9c show that the reaction orders for the dehydration/decarbonylation and dehydrogenation/ decarboxylation reactions were fractional with respect to formic acid, thus necessitating its inclusion in the sight blocking term as well.

The experimental data of this study for the liquid-phase decomposition of formic acid can be described by the rate expressions in Eqs. (1)-(3),

$$r_{\rm co} = k_{\rm co} P_{\rm FA} \Theta_*^2 \tag{1}$$

$$r_{\rm CO_2} = k_{\rm CO_2} P_{\rm FA} \Theta_*^3 \tag{2}$$

$$r_{\rm WGS} = k_{\rm WGS} P_{\rm CO}^{0.125} P_{\rm H_2O} \left( 1 - \frac{P_{\rm CO_2} P_{\rm H_2}}{K_{\rm eqm, WGS} P_{\rm CO}^{0.125} P_{\rm H_2}} \right)$$
(3)

$$\Theta_* = \frac{1}{1 + K_{\rm CO}P_{\rm CO} + \sqrt{K_{\rm H_2}P_{\rm H_2}} + K_{\rm FA}P_{\rm FA}} \tag{4}$$

$$K_i = \exp\left(\frac{-\Delta G_i}{RT}\right) \tag{5}$$

$$\Delta G_{\rm CO} = \Delta G_{\rm CO}^{\rm o} + 0.75 \frac{P_{\rm CO}}{P_{\rm ref}} RT \tag{6}$$

where  $r_{CO}$  is the rate of the dehydration/decarbonylation reaction,  $r_{CO2}$  is the rate of the dehydrogenation/decarboxylation reaction,  $r_{WGS}$  is the rate of the water–gas shift reaction,  $P_i$  is the partial pressures of species *i*,  $K_i$  is the adsorption equilibrium coefficient for species *i*,  $\Delta G_i$  is the free energy of adsorption for species *i*,  $K_{eqm,WGS}$ is the equilibrium constant of the water–gas shift reaction,  $\theta_*$  represents the vacant sites on the catalyst,  $P_{ref}$  is the reference pressure at standard conditions, *R* is the universal gas constant, *T* is the reaction temperature, and 0.75 is a parameter fit for this model. These rate expressions imply the following rate controlling steps for formic acid decomposition

$$FA + 2\theta_* \to CO + H_2O \tag{7}$$

$$FA + 3\theta_* \rightarrow CO_2 + H_2$$
 (8)

where formic acid requires two and three vacant sites in the dehydration/decarbonylation and dehydrogenation/decarboxylation reactions, respectively. The different orders with respect to the vacant sites were determined empirically to describe the dependence of the rates on the partial pressure of formic acid (Fig. 9c). A justification for the different dependence of  $r_{CO}$  and  $r_{CO2}$  on the fraction of vacant sites is that decarbonylation may take place by the reaction of a monodentate carboxyl species with an adjacent vacant site, and decarboxylation may take place by reaction of a bidentate formate species with a vacant site. Additionally, the low order (approximately 0.1) with respect to CO partial pressure for the rate of WGS was determined empirically, because the apparent rate of WGS varied little when the initial partial pressure of CO was varied. This value was the highest fractional order that could be assigned without the model violating the experimentally observed result of net CO production. A low order with respect to CO was also observed experimentally in results communicated to us by Mehta and Ribeiro for their work currently in progress on liquid-phase water-gas shift over a PtMo/C catalyst [52]. Also, we note that the solvent, in this case water, does not appear in the site blocking term, because its partial pressure, and hence its coverage, was constant throughout the experiments. Accordingly, it was lumped with the reaction rate constants to decrease the number of model parameters. Similarly, a reaction order of 1 with respect to water in the WGS rate expression was used because of the nearly constant partial pressure of water.

The reaction rate constants for formic acid and butyl formate were described using the Arrhenius form shown in Eq. (9), and the water–gas shift rate constant was described using Eq. (10):

$$k_i = k_o \exp\left(\frac{-E_a}{RT}\right) \tag{9}$$

$$k_i = k_o \exp\left(\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{avg}}}\right)\right) \tag{10}$$

where  $k_i$  is the reaction rate constant,  $k_o$  is the pre-exponential factor,  $E_a$  is the reaction activation energy, R is the gas constant, T is the temperature of the reaction, and  $T_{avg}$  is the average temperature of the data set. The alternative expression for the WGS rate constant was used because it is a more efficient parameterization for numerical optimization. This mathematical form decouples the effect of the activation energy and pre-exponential factor on the overall rate constant. We have employed this approach for the WGS rate con-



**Fig. 10.** TOF versus temperature for decomposition of (a) FA and (b) BF plus the FA impurity. Solid points show experimental data for decarboxylation/dehydration (■) and decarbonylation/dehydrogenation (♦). Solid lines show predictions of the kinetic model.

stant because we are using an empirical rate expression for this reaction, in contrast to using a mechanistically based rate expression. Fig. 10a shows the experimentally determined activation energies, along with the experimental and model-predicted values of TOF for decomposition of formic acid with respect to temperature and Fig. 10b shows data for the decomposition of BF. (A kinetic model for the decomposition of BF will be addressed later in this paper.)

The relative values of the activation energies for the decomposition of formic acid versus the decomposition of butyl formate indicate that the high CO<sub>2</sub> selectivity for formic acid decomposition is dominated by the change in activation energy of the decarboxylation pathway (from 88 kJ/mol to 67 kJ/mol) upon changing the functional group from the ester to carboxylic acid, while the activation energy of the decarbonylation pathway remains relatively unchanged (from 85 kJ/mol to 88 kJ/mol). This change in activation energy may indicate that the formate species thought to be responsible for production of CO<sub>2</sub> is more readily produced from the acid than the ester, whereas the presence of an ester functional group has a potentially small stabilizing effect on the formation of a potential carboxyl intermediate. The values of  $E_a$  and  $k_o$  are listed in Table 2. Experimental values of activation energies and approximate pre-exponential factors were extracted from plots of experimental data and used as initial guesses for the model. The uncertainties of these values are reported as the standard error of the slope and the standard error in the y-intercept of Fig. 10, respectively, as calculated by the LINEST function of Excel. The approximate pre-exponential factor was calculated by dividing the y-intercept of Fig. 10 by the respective partial pressure and surface vacancy terms from Eqs. (1), (2), (11), and (12). A value of 0.66 was used for the vacancy term as it was a value typical of the initial vacancy according to the model calculations. The model activation energies, pre-exponential factors, and free energies of adsorption were treated as model parameters and optimized using the 'nlinfit'

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Table 2 Pre-exponential factors and activation energies for model reactions.

Parameter	Model $k_o^a$	Model <i>E<sub>a</sub></i> (kJ/mol)	Approximate $k_o^c$	Experimental <i>E<sub>a</sub></i> (kJ/mol)
k <sub>BF,CO</sub> k <sub>BF,CO2</sub> k <sub>WGS</sub> <sup>b</sup> k <sub>FA,CO</sub> k <sub>FA,CO2</sub>	$\begin{array}{c} 1.6 \pm 0.1 \times 10^8 \\ 5.2 \pm 0.1 \times 10^7 \\ 3.1 \pm 0.1 \times 10^{-4} \\ 4.3 \pm 0.9 \times 10^9 \\ 5.7 \pm 0.1 \times 10^8 \end{array}$	$85.3 \pm 0.4 \\ 88 \pm 1 \\ 90 \pm 30 \\ 88 \pm 1 \\ 67 \pm 1$	$\begin{array}{c} 1.5 \pm 0.1 \times 10^8 \\ 6.6 \pm 0.5 \times 10^7 \\ \text{N/A} \\ 2.49 \pm 0.08 \times 10^9 \\ 5.2 \pm 0.2 \times 10^8 \end{array}$	86 ± 3 87 ± 5 N/A 88 ± 2 67 ± 3

The units for  $k_o$  are atm s<sup>-1</sup> except for  $k_{WGS}$ , which has units of atm<sup>1.125</sup> s<sup>-1</sup>. b

 $k_{\text{WGS}}$  was not measured experimentally.

The approximate value of  $k_0$  was calculated for comparison with the model using  $\theta_*$  of 0.66, typical of initial vacancies calculated by the model.



Fig. 11. Rectification plots of the (a) conversion and (b) selectivity for the decomposition of FA at various space velocities in He ( $\bigcirc$ ) and 35% H<sub>2</sub> in He ( $\triangle$ ), at different temperatures ( $\bigcirc$ ), and for different partial pressures of FA ( $\chi$ ), CO (+), and  $H_2$  ( $\square$ ). The values of the parameters used in the model are given in Tables 2 and 3

function of MATLAB, and the uncertainties of the optimized parameters were calculated with the 'nlparci' function.

The rectification plot of Fig. 11 demonstrates the ability of the simplified model to predict the experimental data for the decomposition of formic acid, assuming the reactor operates as a PFR. In particular, it demonstrates the ability of this model to correctly predict the trends in selectivity observed during the space velocity studies and reaffirms the conclusion that these trends are evidence of the secondary role of the water-gas shift reaction in determining the selectivity of CO<sub>2</sub> versus CO compared to the primary role of the direct decomposition pathways. Further evidence for the secondary role of water-gas shift is provided by Fig. 12a, which shows that the ratio of the primary decomposition pathway to the water-gas shift rate is greater than 100 even at conversions of formic acid higher than 90% where WGS would have its largest effect. Finally, the model allows the calculation of the rates at the inlet of the reactor, corresponding to the infinite space velocity condition. The calculated CO<sub>2</sub> selectivity (97.5%) of 2 M formic acid in water at 423 K agrees very well with the value predicted experimentally (97.2%). The values of the adjustable parameters used in the model are provided in Tables 2 and 3.



Fig. 12. (a) Ratio of the decarboxylation rate of FA to the WGS rate calculated by the kinetic model, plotted versus the fractional distance along the PFR. (b) Ratio of the decarbonylation rate of BF to the WGS rate calculated by the kinetic model, plotted versus the fractional distance along the PFR.

Analogous to the reaction order studies in Fig. 9 for the decomposition of formic acid, we carried out reaction order studies for the decomposition of butyl formate. Fig. 13 shows the turnover frequency for the decomposition of butyl formate versus the partial pressures of H<sub>2</sub>, CO, and BF along with the results from the kinetic model that is described below. Note that the trends in the TOF for  $CO_2$  production in these plots are dominated by the amount of  $CO_2$ produced from the formic acid impurity, which reacts to complete conversion and leads to nearly zero order with respect to CO partial pressure and the strong positive reaction order with respect to butyl formate (and consequently formic acid) partial pressure.

The experimental data of Figs. 10b and 13 were used to formulate a kinetic model for the decomposition of BF by adding the following rate expressions to the rate expressions described previously for the decomposition of formic acid (the latter of which were needed to account for the formic acid impurity in the feed),

$$r_{\rm co} = k_{\rm co} P_{\rm BF} \Theta_*^2 \tag{11}$$

$$r_{\rm CO_2} = k_{\rm CO_2} P_{\rm BF} \Theta_*^3 \tag{12}$$

and the site vacancy term was modified to account for the presence of butyl formate on the surface.

$$\Theta_* = \frac{1}{1 + K_{\rm CO}P_{\rm CO} + \sqrt{K_{\rm H_2}P_{\rm H_2}} + K_{\rm FA}P_{\rm FA} + K_{\rm BF}P_{\rm BF}}$$
(13)

The temperature dependence of each rate constant was described with an Arrhenius expression (Eq. (9)). The values of the additional parameters are listed in Tables 2 and 3. The model was solved assuming the parameters from the formic acid model were constant, and only the new parameters for butyl formate were allowed to vary. Fig. 10b shows that the kinetic model captured the trends of the experimental data versus reaction temperature. The rectification plot of Fig. 14 shows that the model describes the

#### Table 3

Values of standard  $\Delta G$  of adsorption for CO, H<sub>2</sub>, BF, and FA calculated by the model.

Species	$\Delta G_{ads}^{o}~(kJ/mol)$
CO <sup>a</sup>	$-0.65 \pm 0.01$
H <sub>2</sub>	$18.0 \pm 0.5$
BF	$-0.55 \pm 0.07$
FA	$-4.6 \pm 0.9$

<sup>a</sup> The model value for  $\Delta G^{0}_{ads,CO}$  is a function of the partial pressure of CO according to Eq. (6). The value in the table is for  $P_{CO}$  equal to 0.



**Fig. 13.** TOF for the decomposition of BF versus partial pressures of (a)  $H_2$ , (b) CO, and (c) BF. Experimental data are given by solid symbols: TOF for decarboxylation ( $\blacksquare$ ) and TOF for decarbonylation ( $\blacklozenge$ ). Solid lines show predictions of the kinetic model. Values of X are reaction orders calculated from experimental data.

experimentally observed trends for the conversion and selectivity for the decomposition of BF versus space velocity, temperature, and the partial pressures of H<sub>2</sub>, CO, and BF. The model demonstrated that the true selectivity of the primary pathway for butyl formate can be found at low space velocity, where the effect of the formic acid impurity is diminished and where forward and reverse WGS are negligible. It was possible with the model to separate the effect that the formic acid impurity had on the CO<sub>2</sub>:CO ratio at infinite space velocity. From the model, it is predicted that the selectivity for the production of CO<sub>2</sub> from 2 M butyl formate in 1-butanol at 423 K is equal to 9.0% for the decomposition of butyl



**Fig. 14.** Rectification plots of the (a) conversion and (b) selectivity for the decomposition of BF at various space velocities in He ( $\bigcirc$ ) and 35% H<sub>2</sub> in He ( $\triangle$ ), at different temperatures ( $\bigcirc$ ), and for different partial pressures of BF (X), CO (+), and H<sub>2</sub> ( $\square$ ). The values of the parameters used in the model are given in Tables 2 and 3.

formate, which gives a  $CO_2$ :CO ratio equal to 1:10. This value agrees favorably with the experimental value of 8.5% selectivity observed at low space velocity. Additionally, Fig. 12b shows that the ratio of the primary decarbonylation reaction was more than 10,000 times greater than the water–gas shift rate throughout the reactor.

#### 4. Conclusions

Palladium supported on carbon was found to be an active, selective, and stable catalyst for the liquid-phase conversion of formic acid and butyl formate. Studies at different space velocities showed that formic acid decomposes primarily through a decarboxylation pathway (leading to  $CO_2$  and  $H_2$ ), whereas butyl formate primarily decomposes through a decarbonylation pathway (leading to CO and butanol). In the presence of water, the formate ester undergoes hydrolysis to form formic acid, which increases the selectivity toward the production of  $CO_2$  and  $H_2$ . When excess water is present,  $CO_2$  and  $H_2$  can be formed with almost quantitative selectivities from butyl formate due to hydrolysis leading to the decomposition of formic acid rather than butyl formate and due to increased water–gas shift activity.

### Acknowledgments

This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences and part of DOE Great Lakes Bioenergy Research Center (www.greatlakesbioenergy.org), which is supported by the US Department of Energy, Office of Science, Office of Biological and Environmental Research, through Cooperative Agreement DE-FC02-07ER64494 between The Board of Regents of the University of Wisconsin System and the US Department of Energy.

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