

Microkinetic Modeling of Benzyl Alcohol Oxidation on Carbon-Supported Palladium Nanoparticles

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Six products are formed from benzyl alcohol oxidation over Pd nanoparticles using O₂ as the oxidant: benzaldehyde, toluene, benzyl ether, benzene, benzoic acid, and benzyl benzoate. Three experimental parameters were varied here: alcohol concentration, oxygen concentration, and temperature. Microkinetic modeling using a mechanism published recently with surface intermediates was able to produce all 18 trends observed experimentally with mostly quantitative agreement. Approximate analytical equations derived from the microkinetic

Introduction

Metal particles can catalyze the liquid-phase oxidation of alcohols directly using O_2 as the oxidant.^[1-4] In particular, benzyl alcohol oxidation to benzaldehyde is of practical use in the pharmaceutical, perfume, dye, and agricultural industries.^[5-6] As a result of this industrial relevance, a number of studies have been conducted on the direct oxidation of benzyl alcohol using Pd-based^[2-4,7-39] and other^[2,13,40-46] coinage and noblemetal catalysts with O_2 as the oxidant. As described elsewhere,^[13] this is considered a green process because O₂ (air) is readily available and the alcohol can be used directly in the reactor without additional solvents or prereactions. Although the main product of benzyl alcohol oxidation is benzaldehyde, five liquid-phase minor byproducts have also been observed: benzene, toluene, benzoic acid, benzyl benzoate, and benzyl ether.^[2, 7, 16, 29, 47] Tentative partial mechanisms were proposed,^[2,4,8–11,29,48–50] and a mechanism with sufficient detail for microkinetic modeling has been published (Scheme 1).^[7]

In this work, we take the next step by performing microkinetic modeling (simulation and fitting) of the reaction. The objectives of this microkinetic modeling are threefold: 1) to provide additional evidence for the mechanism used by verifying that kinetic modeling with this mechanism can reproduce the kinetic behavior observed experimentally (absolute quantities

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model for isothermal conditions reproduced the isothermal trends and provided insight. The most important activation energies are $E_{a2} = 57.9 \text{ kJ mol}^{-1}$, $E_{a5} = 129 \text{ kJ mol}^{-1}$, and $E_{a6} = 175 \text{ kJ mol}^{-1}$, which correspond to alcohol dissociation, alkyl hydrogenation, and the reaction of alkyl species with alkoxy species. Upper limits for other activation energies were identified. The concepts of a sticking coefficient and steric factor in solution were applied.

produced and selectivity trends), 2) to identify which reactions are the most kinetically significant, and 3) to extract kinetic parameters for use in future modeling/studies. The activation energies obtained are in ranges consistent with experiments with benzyl alcohol^[14,48,51-55] on Pd-based surfaces and consistent with experiments with other alcohols^[4,54,56-67] on coinage metals. The microkinetic modeling in this work was able to reproduce the selectivities and trends observed for the production of both the main product (benzaldehyde) and the byproducts (benzene, toluene, benzoic acid, benzyl benzoate, and benzyl ether).

The results and conclusions of this study provide additional support for the mechanism shown in Scheme 1 and provide most of the mechanistic and chemical kinetic information necessary to model of benzyl alcohol oxidation under arbitrary relevant conditions.

Results and Discussion

Microkinetic model

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The experimental data were collected by using a semibatch reactor under transient (unsteady) conditions such that the liquid-phase alcohol concentration and product concentrations varied as a function of time (as in a conventional batch reactor) and the gas-phase O₂ concentration was kept constant (Experimental Section). Several aspects of the reaction conditions were varied (initial alcohol concentration, gas-phase O₂ concentration, and temperature). The conditions investigated are shown in Table 1. The mechanism that the microkinetic model is based on is from a previous study.^[7] The corresponding rate equations and reduced chemical reactions are shown in Table 2. The chemical equations in Table 2 are "net" stoichiometric equations, the rate equations in Table 2 are reflective of



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Scheme 1. Mechanism with sufficient detail for microkinetic modeling. This image has been adapted from Reference [7] with permission from Wiley-VCH.

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Table 1. Experimental conditions investigated. ^[a]					
Experiment	Initial alcohol concentration [vol%]	[O2] [bar]	<i>Т</i> [°С]		
1	25	1.0	70		
2	50	1.0	70		
3	75	1.0	70		
4	25	0.0	70		
5	25	0.25	70		
6	25	0.50	70		
7	25	1.0	70		
8	25	1.0	80		
9	25	1.0	90		
10	25	1.0	100		
[a] Experiment 7 is the same run as 1 and was also used as a data point in the series in which the temperature was varied.					

rate-limiting elementary steps, and additional details are provided in the Supporting Information. An example simulation is shown in Figure 1.

Previous work showed that although the selectivity between toluene and the aldehyde changed as a function of conditions, that the transient kinetics between these two species tracked well if the production of the species was scaled.^[7] In the context of the reaction mechanism shown in Scheme 1, the competition between aldehyde and toluene formation suggests that the aldehyde and the toluene have a common intermediate and there is a pre-equilibrium between the precursor intermediates (in this case, the alkyl and alkoxy intermediates that have a pre-equilibrium defined by the rate constants k_4 and k_{11}). This sets an expectation that k_4 and k_{11} will be $\gg k_3$, k_5 , and k_7 . Based on the transient data reported in Ref. [7] for experiment 4, we anticipate that the intrinsic rate of toluene production is greater than that of ether production such that we expect $k_5 > k_6$. The transient kinetics in Ref. [7] also showed evidence that for the carbonyloxyl pathway (which leads to benzene, benzoic acid, and benzyl benzoate), the formation of car-



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Figure 1. Transient kinetic profiles for the six product concentrations at 80 °C with 1 bar of O_2 and an initial alcohol concentration of 2.32 mol L⁻¹. Filled symbols are from the full microkinetic model using the parameters in Tables 3 and 4. Open symbols are from experiments in Ref. [7].

bonyloxyl was rate-limiting followed by fast conversion to these three products, accordingly, we anticipate that k_{8} , k_{9} , $k_{10} \gg k_7$. DFT calculations^[68] of the relevant activation energy

Table 2. Reduced chemical equations and rate equations.				
Reaction	Reduced chemical equation	Rate equation*		
1	$O_2 + 2S \rightarrow 2O - S$	$R_1 = 2k_1[S][S][O_2]$		
2	Alcohol + S + $O-S \rightarrow Alkoxy-S + HO-S$	$R_2 = k_2$ [Alcohol][O-S][S]		
3	Alkoxy–S + HO–S + S \rightarrow Aldehyde + H ₂ O + 3 S	$R_3 = k_3 [Alkoxy - S][S]$		
4	Alkoxy–S + HO-S + 2S \rightarrow Alkyl–S + 2O–S + H–S	$R_4 = k_4 [Alkoxy - S][S]$		
5	Alkyl-S + 2O-S + H-S \rightarrow Toluene + 2O-S + 2S	$R_{\rm S} = k_{\rm S} [\rm Alkyl-S][\rm H-S]$		
6	Alkyl–S + O–S + H–S + Alkoxy–S + OH–S \rightarrow	$R_6 = k_6 [Alkoxy - S][Alkyl - S]$		
	Ether $+ O - S + H_2O + 4S$			
7	Alkoxy–S + OH–S + O–S + 2 S \rightarrow	$R_7 = k_7 [Alkoxy - S][O - S][S]$		
	Carbonyloxyl-SS + $HO-S$ + $2H-S$			
8	Carbonyloxyl–SS + HO–S + 2H–S \rightarrow	$R_8 = k_8$ [Carbonyloxyl–SS][H–S]		
	Benzene + CO_2 + H_2O + $4S$			
9	Carbonyloxyl-SS + HO-S + 2H-S \rightarrow	$R_9 = k_9$ [Carbonyloxyl–SS][H–S]		
	Benzoic Acid $+ H_2O + 4S$			
10	Carbonyloxyl-SS + 2HO-S + 2H-S + Alkoxy-S \rightarrow	$R_{10} = k_{10}$ [Carbonyloxyl–SS][Alkoxy–S]		
	Benzylbenzoate $+ 2H_2O + O-S + 6-S$			
11	Alkyl–S + 2O–S + H–S \rightarrow	$R_{11} = k_{11} [Alkyl - S][O - S]$		
	Alkoxy-S + OH-S + 2S			
*[S] indicates a surface species that occupies one site and [SS] indicates a surface species that occupies two surface sites.				

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barriers over Pd suggest that the barriers for $HO_{(ads)}+H_{(ads)}$ to form H_2O are smaller than those of $HO_{(ads)}$ and that the rate constants calculated for this process are higher than those that are rate-limiting in this study (Table 3).

Table 3. Fitted rate constants from microkinetic model at 70 °C.			
k	Value		
k ₁	$8.2 \times 10^{\circ} \text{ s}^{-1} \text{ bar}^{-1}$		
k ₂	$1.4 \times 10^{-1} \text{ s}^{-1} \text{ mol}^{-1} \text{ L}$		
k ₃	$5.1 \times 10^{6} \text{ s}^{-1}$		
<i>k</i> ₄	$6.7 \times 10^8 \text{ s}^{-1}$		
k₅	$4.4 \times 10^{14} \text{ s}^{-1}$		
k ₆	$2.9 \times 10^{11} \text{ s}^{-1}$		
k ₇	$1.6 \times 10^6 \text{ s}^{-1}$		
k ₈	$1.4 \times 10^{14} \text{ s}^{-1}$		
k ₉	$5.5 \times 10^{14} \text{ s}^{-1}$		
k ₁₀	$9.4 \times 10^{12} \text{ s}^{-1}$		
k ₁₁	$2.2 \times 10^{11} \text{ s}^{-1}$		

Based on the forking of the reaction mechanism and given that the production of species varied across several orders of magnitude, such that the rates of production at 70 °C were aldehyde \geq toluene \geq benzyl ether ~ benzene ~ benzoic acid ~ benzyl benzoate, the system was conducive towards sequential parameter optimization using the data from the experiments at 70 °C. Sequential parameter optimization was performed in the order of (k_1, k_2, k_3) , $(k_4/k_{11}, k_5)$, (k_6) , (k_7) , (k_8) , (k_9) , (k_{10}) , (k_7, k_8, k_9, k_{10}) followed by refinement. The parameters obtained are shown in Table 3 and are in line with the expectations described above. The rate constants associated with the surface reactions do not exceed the limits associated with physically realistic pre-exponentials.^[69-75] The simulated end-ofexperiment selectivities are shown in Figures 2 and 3 as a



Figure 2. Selectivities for the six products as a function of initial alcohol concentration with one bar of O_2 . The filled black squares are from experiment, the open red circles are from simulation by the microkinetic model, and the open green triangles are from simulation using approximate analytical expressions derived from the microkinetic model.

function of the changing alcohol and oxygen concentrations. All of the trends observed in the experimental data are reproduced by the microkinetic model (Figures 2 and 3), and most of the agreement is quantitative for the selectivities at the end of the experiment. The deviation observed for the benzoate





Figure 3. Selectivities for the six products as a function of gas-phase O_2 concentration from the experiment, microkinetic modeling, and approximate analytical expressions. Symbols as in Figure 2.

may be caused by a coverage-dependent activation energy, whereas the more significant deviation observed for the ether could be because of local ensemble configurations that would require kinetic Monte Carlo methods^[76–78] for accurate simulation. Notably, because the microkinetic model involves physically realistic constraints, the rate constants in Table 3 fall within the literature guidelines of the physically realistic limits for rate constants of reactions on surfaces. A further method to gain insight is to derive approximate analytical expressions from the microkinetic model to verify the physical reasonableness of the model.

Approximate analytical expressions for responses from the microkinetic model

To derive approximate analytical expressions for the responses (rates of product formation) we wrote expressions for the rate equations. Except for the terms [Alcohol] and $[O_2]$, all of the concentrations that appear on the right-hand side of the expressions below refer to surface concentrations. In these equations, [S] refers to the relative coverage of open surface sites, and [O] refers to the relative coverage of adsorbed oxygen atoms. First, we start with the pre-equilibrium as that is an easy step to write and can be used to simplify later expressions [Eq. (1)]:

$$k_4[\text{Alkoxy}][\text{S}] = k_{11}[\text{Alkyl}][\text{O}] \tag{1}$$

Next, we assume that after adsorption the oxygen and alcohol are consumed primarily by reactions, which is consistent with the data and the literature,^[52,53] to give [Eqs. (2) and (3)]:

$$\frac{d[Alcohol]}{dt} = -k_2[S][O][Alcohol]$$
(2)

$$\frac{d[O]}{dt} = k_1[S][S][O_2] - k_2[S][O][Alcohol] + ...$$
(3)

The surface oxygen is (by stoichiometry) consumed primarily by alkoxy creation, and the alkoxy intermediate concentration can be described by a quasi-steady-state approximation [Eq. (4)]:

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$$\frac{d[Alkoxy]}{dt} = k_2[S][O][Alcohol] - k_3[S] - k_4[S][Alkoxy] + k_{11}[O][Alkyl]$$
(4)

The term with k_3 is associated with aldehyde production, whereas the terms with k_4 and k_{11} are associated with the preequilibrium towards toluene. As aldehyde production \gg toluene production at this temperature, the sum of the k_4 and k_{11} terms should be much less than the k_3 term and can be neglected if we estimate the quasi-steady-state alkoxy concentration. The validity of this approximation was checked by plotting ([Alcohol]–[Alcohol]_f) versus time and –([Aldehyde]–[Aldehyde]_f) versus time, and the plots matched very well. If we solve for the alkoxy concentration we obtain [Eq. (5)]:

$$[Alkoxy] \approx \frac{k_2[S][O][Alcohol]}{k_3[S]} = \frac{k_2[O][Alcohol]}{k_3}$$
(5)

from Equation (1), we can now solve for the alkyl concentration [Eq. (6)]:

$$[\mathsf{Alkyl}] \approx k_4 \left(\frac{k_2[\mathsf{O}][\mathsf{Alcohol}]}{k_3}\right) \frac{[\mathsf{S}]}{k_{11}[\mathsf{O}]} = \frac{k_4 k_2}{k_3 k_{11}} [\mathsf{Alcohol}][\mathsf{S}] \tag{6}$$

If we write the differential equations for aldehyde and toluene production we find [Eqs. (7) and (8)]:

$$\frac{d[Aldehyde]}{dt} \approx k_3[S]\left(\frac{k_2[O][Alcohol]}{k_3}\right) = k_2[S][O][Alcohol]$$
(7)

$$\frac{d[\text{Toluene}]}{dt} \approx k_5 \frac{k_4 k_2}{k_3 k_{11}} [\text{Alcohol}][\text{S}]$$
(8)

Interestingly, the aldehyde production rate is ultimately proportional to k_2 even though the reaction for aldehyde production is associated with k_{3} , which is consistent with the literature. $^{\left[13,53,66,67,79\right]}$ If we look at the above equations, we see that the concentration dependences are consistent with the experimental observations. First, as described in Equation (5), plots of the aldehyde production and alcohol concentration depletion corresponded, which is consistent with Equations (2) and (7) and differs by only a negative sign. Second, Equations (7) and (8) show that for a given oxygen pressure and temperature, the toluene production should be proportional to the aldehyde production. Third, the difference of the [O] between Equations (7) and (8) indicates that with increasing oxygen the selectivity ratio should favor aldehyde production over toluene production in a way that is roughly first order with surface oxygen, which in turn is roughly first order with oxygen pressure by rearrangement of Equation (3). These three implications are all consistent with the experimental results.^[7]

If we solve for the ether production we obtain [Eq. (9)]:

$$\frac{d[\text{Ether}]}{dt} \approx k_6 \left(\frac{k_2[S][O][\text{Alcohol}]}{k_3[S]}\right) \frac{k_4 k_2}{k_3 k_{11}} [\text{Alcohol}][S]$$
(9)

If we apply the steady-state approximation to the concentration of the carbonyloxyl species we obtain the following relationships for the products from that pathway [Eqs. (10)–(12)]:

$$\frac{\mathsf{d}[\mathsf{Benzene}]}{\mathsf{d}t} \approx k_8 \frac{k_7 k_2 [\mathsf{Alcohol}][\mathsf{O}]^2}{k_8 + k_9 + k_{10} \frac{k_2 [\mathsf{O}] (\mathsf{Alcohol}]}{k_3}} \tag{10}$$

$$\frac{\mathrm{d}[\mathrm{Benzoic Acid}]}{\mathrm{d}t} \approx k_9 \frac{k_7 k_2 [\mathrm{Alcohol}][\mathrm{O}]^2}{k_8 + k_9 + k_{10} \frac{k_2 [\mathrm{O}][\mathrm{Alcohol}]}{k_3}}$$
(11)

$$\frac{\mathrm{d}[\mathrm{Benzoate}]}{\mathrm{d}t} \approx k_{10} \left(\frac{k_2[\mathrm{O}][\mathrm{Alcohol}]}{k_3}\right) \frac{k_7 k_2[\mathrm{Alcohol}][\mathrm{O}]^2}{k_8 + k_9 + k_{10}\frac{k_2[\mathrm{O}][\mathrm{Alcohol}]}{k_3}} \quad (12)$$

Unsurprisingly, we see that the carbonyloxyl pathways all depend on k_7 , k_8 , k_9 , and k_{10} . We also see that the benzoate production has a higher order [O] dependence relative to the benzene and benzoic acid productions, which was shown experimentally.^[7]

Additional microkinetic simulations were performed using these approximate analytical expressions for the rates of product formation rather than using the directly simulated rates of product formation. Sequential parameter optimization was performed as before. The approximate analytical expressions are also able to produce most of the trends with near quantitative agreement (Figures 2 and 3). This provides additional evidence for the mechanism used as well as our understanding of the implications of the mechanism and the operative kinetics. The rate constants derived from this sequential parameter optimization are compared in Figure 4 to those obtained from



Figure 4. Comparison of rate constants obtained by sequential parameter optimization during simulation and fitting using the microkinetic model versus those using the analytical approximations for the rates of production of the products on top of the microkinetic model.

sequential parameter optimization with the microkinetic model. The trends of the rate constants are generally preserved, whereas k_5 and k_6 are altered because the use of approximate analytical expressions introduces inaccuracies that result in different alkoxy concentrations between the two types of simulations.



The fact that the analytical equations derived from approximations to the microkinetic model can also reproduce the trends and values observed for the selectivities provides additional evidence that the mechanism and microkinetic model rate equations are correct. Additionally (and perhaps more importantly), the analytical equations enable us to see which rate constants and concentrations are most important for a given product. As can be seen from the equations above, the rates of formation of the various products are generally affected by more than one rate constant. As can also be seen, the rates of production of all of the products scale directly with k_2 , which is the rate of alcohol adsorption. The fact that the rates of production for all products scale with k_2 is not clear from the data given in Table 3 but is clear from the equations above.

Temperature dependence

After we had obtained fitted rate constants for the microkinetic model at 70 °C, the next step was to investigate the temperature dependence. By calling the fitted rate constants at 70 °C base rate constants ($k_{i,b}$) at a base temperature (T_b), we can define the rate constants at all temperatures relative to the rate constants at 70 °C. The pre-exponentials are considered to be independent of temperature. In this case, the rate constants for a particular temperature T_x are given by [Eq. (13)]:

$$k_{x} = k_{b} e^{\left[\left(-\frac{E_{x}}{RT_{x}}\right) - \left(-\frac{E_{x}}{RT_{b}}\right)\right]} = k_{b} e^{-\frac{E_{x}}{R}\left[\left(\frac{1}{T_{x}}\right) - \left(\frac{1}{T_{b}}\right)\right]}$$
(13)

in which $k_{\rm b}$ is the base rate constant for a given reaction at $T_{\rm b}$, $k_{\rm x}$ is the rate constant for that reaction at the temperature measured $(T_{\rm x})$, $E_{\rm a}$ is the activation energy of reaction, which is considered to be independent of temperature, and R is the ideal gas constant.

We begin by assuming that the oxygen adsorption step (which corresponds to k_1) has a smaller activation energy than the rate-limiting reaction/desorption steps, which is a reasonable assumption for surface reactions and is consistent with the literature. The initial rates of production of the three major products, aldehyde, toluene, and ether, were each found previously to have a strong dependence on temperature.^[7] A plot of the natural log of the initial rates of formation for aldehyde



Figure 5. Arrhenius-type plot with the natural log of the early-time TOF vs. 1/*T* for benzaldehyde formation and toluene formation. Apparent activation energies were extracted from the slopes.

and toluene (in units of the turnover frequencies (TOFs) from the time range where the production was approximately linear with time) are shown in Figure 5, and the fitting of the slopes provided estimated apparent activation energies of 57.9 and 129 kJ mol⁻¹, respectively. The apparent activation energy for the aldehyde formation is consistent with that in the literature,^[14,48,51-53] and the separate apparent activation energy for toluene formation is consistent with the conclusion of a previous study^[52] that the toluene formation is reaction limited. From these fits, the following relationships can be written for 70 °C under the conditions studied for the initial rates: In(TO- $F_{aldehyde} s^{-1} = (-57.9 \text{ kJ mol}^{-1})/RT + 27.6 \text{ and } \ln(TOF_{toluene} s^{-1}) =$ $(-129 \text{ kJmol}^{-1})/RT+49.8$. The apparent activation energy for the aldehyde production should be reflective of k_2 rather than k_3 . This was borne out by our unabridged microkinetic simulations: if we set $E_{a3} = 57.9 \text{ kJ mol}^{-1}$ there was nearly no change for the simulation at any temperature. If we set $E_{a2} =$ 57.9 kJ mol⁻¹ and $E_{a5} = 129$ kJ mol⁻¹ it was sufficient to reproduce a surprisingly high number of the experimental features at all temperatures studied. The construction of similar plots with the ether production using early-time data and final data showed that the best fit for the activation for the ether production was between 140 and 211 kJ mol⁻¹.

As the rate of reaction increases with temperature, the temperature dependence was fitted using the absolute production of the full microkinetic model at the 30 min mark using all temperatures simultaneously: the 30 min data points were kinetically relevant for the selectivity at all temperatures studied. During parameter optimization using the temperature-dependent data, the temperature dependence was described with the rate constants referenced to the 70 °C rate constants (i.e., in the equations above, T_b =70+273.15 K). During this optimization, the initial guess for the term [Eq. (14)]

$$\mathbf{e}^{-\frac{E_{a}}{R}\left[\left(\frac{1}{T_{x}}\right)-\left(\frac{1}{T_{b}}\right)\right]}$$
(14)

is 1. As the activation energy optimization occurs relative to the rate constants of the base temperature, this initial guess corresponds to using the 70 °C rate constant values as the best initial guess for all temperatures (it does not imply a lack of temperature dependence or lack of activation energy). If we



Figure 6. Concentrations of the six species produced after 30 min in a transient-mode semibatch reactor as a function of temperature. The filled black squares are from experiment and the open red circles are from simulation by the microkinetic model.

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run the full microkinetic model and use the data points in Figure 6 (using all temperatures studied) with gradient optimization based on the weighted sum of squared residuals of those points we obtained a value of $E_{a6} = 175 \text{ kJ mol}^{-1}$ if the initial value for E_{a6} was either 140 or 211 kJ mol⁻¹. The fitted values for E_{a2} , E_{a5} , and E_{a6} are reported in Table 4.

Table 4. Fitted values and upper limits for the activation energies ofeach reaction determined from simulations.				
Ea	Fitted value [kJ mol ⁻¹]	Determined upper limit [kJ mol ⁻¹]		
E _{a1}	-	<130		
E _{a2}	57.9	< 90		
E _{a3}	-	<120		
E _{a4}	$0.96(E_{a11})+12$	-		
E _{a5}	129	< 240		
E _{a6}	175	< 270		
E _{a7}	-	<60		
E _{a8}	-	< 60		
<i>E</i> _{a9}	-	<40		
<i>E</i> _{a10}	-	< 120		
<i>E</i> _{a11}	1.04(<i>E</i> _{a4})-12	-		

The simulated temperature dependence of the data with these three activation energies set as described and all other reactions simulated with no temperature dependence (e.g., k_{10} at 100 °C is the same as k_{10} at 70 °C) is shown in Figure 6. The microkinetic model is able to reproduce all of the trends and absolute quantities near those observed for product formation. It is especially interesting that our model reproduces not only any observed product formation increases with temperature but also the observed product formation decreases with temperature. This observation can be interpreted to mean that k_{2r} k_{5} , and k_{6} dominate the temperature dependence of the overall rates and selectivities of the reactions in the system. The activation energies of the other reactions are less important for the temperature dependence and likely smaller in value. Estimated values for the activation energies of the other reactions could not be determined as the fit is already sufficiently good that no significant improvement could be obtained by varying the other activation energies. However, upper limits for the activation energy of most of the reactions were able to be determined by a local sensitivity analysis (limits shown in Table 4). The local sensitivity analysis was performed by starting with the final parameters and then an individual activation energy was increased until the weighted sum of squared residuals doubled for either the data points that correspond to all six products or for the data points that correspond to all of the products of the pathway associated with that rate constant. For k_4 and k_{11} , if one activation energy was varied, the complementary activation energy was allowed to reoptimize as these reactions exist as a pre-equilibrium (i.e., if E_{a4} was changed, E_{a11} was allowed to vary and vice versa). We anticipated that we would be able to determine separate upper limits for E_{a4} and E_{a11} but instead we found an approximately linear empirical relationship between E_{a4} and E_{a11}, such that E_{a11} \approx 1.04(E_{a4})-12 kJ mol⁻¹ and conversely E_{a4} \approx 0.96(E_{a11})+12 kJ mol⁻¹. The estimated upper limits and relationships determined for the rate constants are provided in Table 4.

Steric factor for sticking from the liquid phase

Given the type of kinetic modeling used here, it should be possible to extract the steric factor^[80,81] for the molecule "sticking" to the surface at the beginning of reaction. This will serve as a check to make sure the model has kinetics that are of a physically realistic order of magnitude. We start with a comparison to gas-solid adsorption. For gas-solid adsorption, the rate of adsorption can be calculated using the gas flux equation from kinetic gas theory combined with a steric factor and an exponential term [Eq. (15)]:

$$R_{ads} = (Flux)S = (Flux)S_0 e^{-Ea/RT}$$
(15)

in which S is the sticking probability, S_0 is the steric factor (as described in collision theory), T is the temperature, E_a is the activation energy of reaction, which is considered to be independent of temperature, and R is the ideal gas constant.^[82] S_0 is fixed between 0 and 1. We will apply the same strategy to the rate of liquid-solid adsorption by calculating a flux for how often a new solute/solvent molecule encounters the surface site. In the liquid phase the collisions are not discrete and are not single collision events, instead they are groups of collisions per "encounter" before the molecules diffuse away from each other.^[82] Partially because of this phenomenon, there have been very few attempts to measure a sticking coefficient for the liquid phase experimentally^[83,84] and only limited attempts to apply collision theory to reactions in liquids.^[85,86] New computational and experimental methods will probably enable the further study of this phenomenon. For the purposes of our study, we will make an estimation of the frequency at which the surface encounters new molecules based on the liquidphase diffusion coefficient and approximate the exchange of positions of molecules in the liquid as movement between 3D locations that are the size of the molecule (i.e., we approximate the nanoscale diffusion as movement between grid points in 3D gridded space, though the same conclusions are reached if continuum diffusion on the molecular scale is assumed). We will assume that adsorption events are rare compared to exchange events between the near surface solution region and bulk solution region (as will be shown, this turns out to be a good assumption for our system).

The frequency for transition between such 3 D locations (i.e., the frequency for exchange between a molecule at the surface and the solvent molecule above it, and thus the flux of new molecules on the surface) can then be obtained from Equation (16):^[87–89]

$$Z = D/d^2 \tag{16}$$

in which Z is the frequency of jumps between positions, d is the distance between positions, and D is the macroscopic dif-

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fusion coefficient. Typical values of D for molecules in liquids are on the order of $\sim 1 \times 10^{-5}$ cm²s⁻¹.^[82-84] To estimate bounds for the value of D, we note that the tabulated value for toluene in benzene is 1.85×10^{-5} cm²s⁻¹, that for phenol in water is 0.89×10^{-5} cm²s⁻¹, and that for 1-butanol in water is $0.56 \times$ $10^{-5} \text{ cm}^2 \text{s}^{-1}$.^[90] We will take bounds of $0.50 \times 10^{-5} - 2.00 \times 10^{-5}$ and calculate the estimated steric factor for each of these bounds. For d, we will use the Stokes diameter of benzyl alcohol to give d = 0.95 nm.^[91] If we use these numbers in Equation (16), we get bounds of $5.5 \times 10^8 < Z < 2.2 \times 10^9 \text{ s}^{-1}$. Interestingly, this is several orders of magnitude smaller (~10³-10⁶ times smaller) than the frequency of pre-exponentials of surface reactions.^[69-75] If we use these values for the flux in Equation (15) along with our extracted values for k_2 , we get an order of magnitude estimate that $0.04 < S_0 < 0.17$, which seems reasonable (and perhaps fortuitously good). Thus, the kinetic parameter values obtained from the microkinetic model also pass this check that they are physically reasonable. As noted in Ref. [82] (p. 318), the diffusion limit for reactions in solution is $\sim \geq 10^{-10}$ s, and the depletion of molecules here is orders of magnitude slower than that.

Conclusions

Benzyl alcohol oxidation over Pd nanoparticles supported on carbon generates six products: benzaldehyde, toluene, benzyl ether, benzene, benzoic acid, and benzyl benzoate. Microkinetic modeling using the mechanism published by Savara et al.^[7] is able to produce all of the trends observed experimentally with mostly quantitative agreement. This corresponds to a total of 18 trends that are reproduced as there are six products and three experimental parameters that varied: alcohol concentration, oxygen concentration, and temperature. In most cases, quantitative agreement was achieved for the product quantities and selectivities obtained by experiment. Additional insights on how the rate constants affect the production of each product (and thus selectivities) were gained from the analytical equations that were derived from the microkinetic model. The present study suggests that the most important activation energies are those of k_2 , k_5 , and k_6 (Scheme 1), which we estimate as $E_{a2} = 57.9 \text{ kJ mol}^{-1}$, $E_{a5} = 129 \text{ kJ mol}^{-1}$, and $E_{a6} =$ 175 kJ mol⁻¹. Upper limits for the activation energies of the other rate constants were also identified (Table 4). For a solution that is 25% benzyl alcohol (2.32 molL⁻¹) under 1 bar O₂, the turnover frequencies (TOFs) for benzaldehyde and toluene production at 70 $^\circ\text{C}$ can be calculated using the empirical relationships $\ln(TOF_{aldehyde} s^{-1}) = (-57.9 \text{ kJ mol}^{-1})/RT + 27.6$ and $ln(TOF_{toluene} s^{-1}) = (-129 \text{ kJ mol}^{-1})/RT + 49.8$, respectively, rather than performing a full microkinetic simulation. The application of the concepts of a sticking coefficient and steric factor in solution yielded a steric factor that was physically reasonable, which is consistent with the kinetic parameters and is physically realistic. The method used to apply the concept of a sticking coefficient and steric factor for liquid-solid adsorption was approximate and is expected to be general.

Experimental Section

The Pd nanoparticle synthesis and characterization details were provided previously.^[7,29] Pd supported on activated carbon (Pd/AC) was prepared by a wet chemical method with a metal-to-support loading of 1 wt%. The particles were characterized by TEM and have a size distribution of 2–8 nm, centered around 4 nm.^[29] The surface Pd comprises 31% of the total Pd atoms (based on Table 2.1 of Ref. [92]), which is within 10% agreement of approximating the particles as spheres for most of the particles in the size distribution used here.

Reactions were performed in a 30 mL glass reactor equipped with a thermostat and an electronically controlled magnetic stirrer. A stirring rate of 1250 rpm was used, which was shown previously to exclude diffusion limitations and to be suitable for chemical kinetic studies. $^{\left[7,9,28,35-36,48\right]}$ The glass reactor was connected by tubing to a mass-flow controller used to flow gas mixtures, with a second port connected by tubing to the building exhaust to enable the continuous flow of gas through the reactor such that the gasphase partial pressures remained constant during the experiment. Thus, the O₂ gas-phase pressure could be used as a proxy for the concentration of O2 in the liquid during kinetic modeling. The gas flow was 30 mLmin⁻¹ and the total pressure was always at 1 bar of O_2 or O_2 diluted by N_2 . We used 60 mg of supported catalyst (0.6 mg of Pd per sample). Benzyl alcohol was premixed with the solvent p-xylene, and the total liquid volume was always kept at 10 mL. Reaction time zero was marked by the beginning of stirring, and the heating to the desired temperature was on the order of minutes, and reactions were monitored with measurements taken at intervals until 120 min after reaction time zero (a total of six measurements per experiment). Each experiment represents 36 data points as there are six product species with concentrations measured six times per experiment. Based on mass balance, little to no liquid-phase reactants and products evaporated during the course of experiment. The TOFs observed in this study are on the order of 1000 molecules per Pd atom per hour, which is in line with literature results.^[13, 24–34, 39]

For microkinetic modeling, it was necessary to translate changes in the liquid-phase concentrations [mol L⁻¹] to units that could be related to the molecules produced per surface site of Pd per unit time. Based on the size distribution^[29] of the particles and the estimated number of surface Pd atoms per particle, $^{\left[92\right]}$ we calculated an estimated 8.2×10¹⁸ atoms of surface Pd in each experiment, and we define this as the amount for one monolayer equivalent (MLE).^[69] The density of benzyl alcohol is 1.045 g mL⁻¹ and it has a molecular weight of 108.138 g mol⁻¹. As the total liquid volume was kept at 10 mL, the number of molecules to produce a change of 1 mol L⁻¹ is equal to 764 MLE. During microkinetic simulations, the surface coverages were represented in the usual way with relative coverage of a given species, θ_i was bound between 0 and 1, and the concentration of empty sites was also bound between 0 and 1. The rates of change for the concentrations of the liquid phase [mol L⁻¹] and of the relative coverages (in unitless relative coverages, θ_i) were calculated accordingly. The rate equations in Table 2 rely upon units as follows: surface species concentrations are in units of theta (unitless relative coverage), gas-phase species concentrations are in bar, and liquid-phase species are in units of molL⁻¹. Simulations were performed using Athena Visual Studio, and fitting was accomplished by sequential parameter optimization aided by gradient based parameter optimization with the objective function defined by the weighted sum of squared residuals. Although local parametric error estimation is possible with gradient optimization,^[93] global (i.e., true) parameter error estimation is

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not possible for multiparameter kinetic fitting in the absence of probability distributions for the values of the parameters.

An example simulation is shown in Figure 1.

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FULL PAPERS



Kinetic modeling: A microkinetic model for benzylic alcohol oxidation based on a recently established mechanism with two major pathways that includes surface intermediates is able to reproduce the experimental data. Analytical approximations of the kinetic model also reproduce the experimental data. Relevant activation energies and kinetic parameters are obtained. A. Savara,* I. Rossetti, C. E. Chan-Thaw, L. Prati, A. Villa



Microkinetic Modeling of Benzyl Alcohol Oxidation on Carbon-Supported Palladium Nanoparticles