

# Benzyl Alcohol Oxidation on Carbon Supported Pd Nanoparticles: Elucidating the Reaction Mechanism

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**Abstract:** Experiments were conducted on the liquid phase oxidation of benzyl alcohol over Pd nanoparticles, with the aim of determining the operative chemical reaction. Experiments were conducted in a batch reactor with para-xylene as the solvent and continuous gas purging of the headspace. The following experimental parameters were varied: the initial benzyl alcohol concentration, the oxygen partial pressure in the headspace, and the reactor temperature. From trends in the concentration profiles and integrated production of each product, it was determined that there are two primary reaction paths: A) an alkoxy pathway leading to toluene, benzaldehyde, and benzyl ether, and B) a carbonyloxy pathway ("neutral carboxylate") leading to benzoic acid, benzene, and benzyl benzoate. From the mechanism elucidated, it is clear that the coverages of atomic hydrogen, atomic oxygen, and surface hydroxyls must be accounted for to achieve a complete description of the quantitative kinetics.

## Introduction

The liquid phase oxidation of alcohols over supported metal catalysts, using molecular oxygen as the oxidant, has been extensively studied in the last decade.<sup>[1-4]</sup> Among the alcohols, benzyl alcohol is one of the most studied substrates.<sup>[2-15]</sup> Depending on the reaction conditions (temperature, solvent, oxygen pressure), many side-products including benzene, toluene, benzoic acid, benzyl benzoate, and benzyl ether have been reported to be formed in addition to the main product, benzaldehyde.<sup>[2, 6, 16-17]</sup> Tentative mechanisms were proposed,<sup>[11, 15-16, 18]</sup> including two mechanisms for the formation of toluene: either by "disproportionation" of benzyl alcohol<sup>[19-21]</sup> or via a geminal diol intermediate formed by reaction with OH or H<sub>2</sub>O.<sup>[4, 22]</sup> However, a detailed and complete mechanism of Pd catalyzed benzyl alcohol oxidation in organic solvent has not yet been published, particularly at a level which would enable microkinetic modeling.

In this study, we have performed experiments in which the temperature, gas-phase oxygen pressure, and initial concentration of the benzyl alcohol were varied in order to elucidate the mechanism. Key insights were also gained from surface science literature of reactions with alcohols and

aldehydes over metal surfaces. There is a long history of studying the reactions of organic molecules on transition metal surfaces,<sup>[23-27]</sup> with elucidation of the mechanisms of reactions at the molecular level. Ultrahigh vacuum studies with small alcohols and aldehydes -- less than four carbons -- on Pd and other transition metal surfaces,<sup>[28-42]</sup> have provided insight into the mechanisms of reactions with organic oxygenates on transition metal surfaces.<sup>[27]</sup> Using the data acquired in this study alongside the information from surface science studies, we elucidate the mechanism of benzyl alcohol oxidation over Pd nanoparticles supported on activated carbon.

## Results and Discussion

Previous experiments were conducted with cyclohexane as a solvent, with the reactant liquid in contact with an oxygen reservoir.<sup>[16]</sup> However, in this temperature range the vapor pressures of cyclohexane and several products are small but not insignificant. The liquid phase for these conditions is on the order of 1000 times more dense than the gas phase: thus if even 1% of the liquid phase evaporates in a static batch reactor, such evaporation can "push away" a significant quantity of oxygen in the absence of a well-mixed system. To keep the oxygen concentration known and constant, we utilize continuous gas flow through the headspace and switched to a lower vapor pressure solvent with low reactivity (para-xylene). In this configuration, some product molecules may still enter the vapor, but are continuously purged from the system by the flowing feed gas, preventing an oxygen-deficient stagnation layer in the gas phase directly above the liquid. Under these conditions, the gas phase oxygen concentration is constant.

Table 1 lists the conditions studied, and the following chemicals were monitored by gas chromatography: benzene, toluene, benzaldehyde, benzyl alcohol, benzoic acid, benzyl ether, benzyl benzoate (these products are shown in Scheme 1). The full set of experimental data is included as supporting information, along with scaled and unscaled kinetic profiles for each species monitored. Fig.1 shows a typical profile from experiment #2, where Fig. 1A.ii is scaled to show the minor products. As can be seen in Fig 1A.i, there is little change in the mass balance of the liquid over time, based upon the sum of the aromatics detected. Under all of the conditions investigated in experiments, the product distribution followed benzaldehyde > toluene > minor products. The minor products detected in the liquid phase consisted of benzoic acid, benzyl ether, benzyl benzoate, and benzene. The ratios and the concentration profiles of the minor products varied as conditions were changed.

At the end of experiment, the final concentration of a given species represents the integrated production during experiment, and is used with varying conditions to gain insight into the reaction mechanism. Note that because the final concentration is an integrated production, we may also convert these numbers to selectivities over the experiment period. Figures 2-4 show

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how the final concentrations and selectivities vary as a function of initial alcohol concentration, oxygen concentration, and temperature. These results will be analyzed and discussed below.

**Table 1.** Experimental Conditions Investigated <sup>[a]</sup>

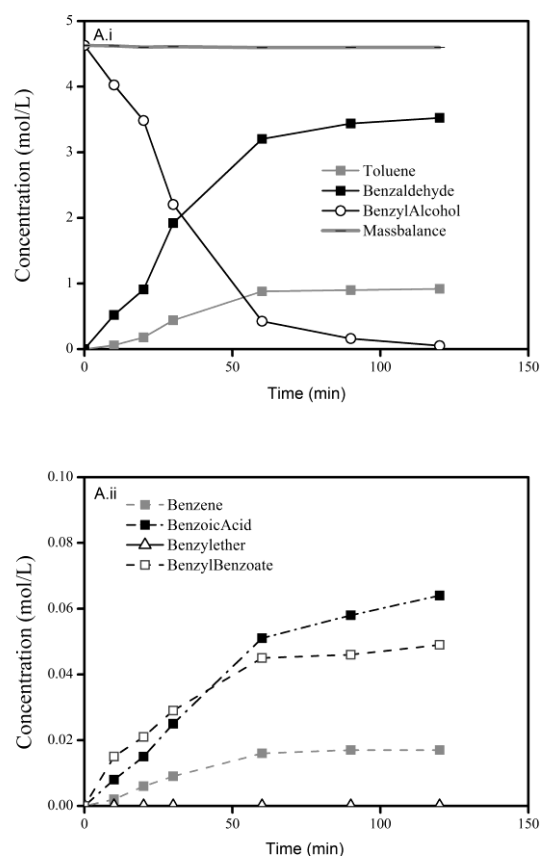
Exp. #	Initial Alcohol Concentration (%V)	[O <sub>2</sub> ]/bar	T (°C)
1	25	1.0	70
2	50	1.0	70
3	75	1.0	70
4	25	0.0	70
5	25	0.25	70
6	25	0.50	70
7	25	1.0	70
8	25	1.0	80
9	25	1.0	90
10	25	1.0	100

<sup>[a]</sup> Exp. #7 is the same run as #1, and was also used as a data point in the series where temperature was varied.

### Alkoxy intermediate for toluene, benzaldehyde, and benzyl ether.

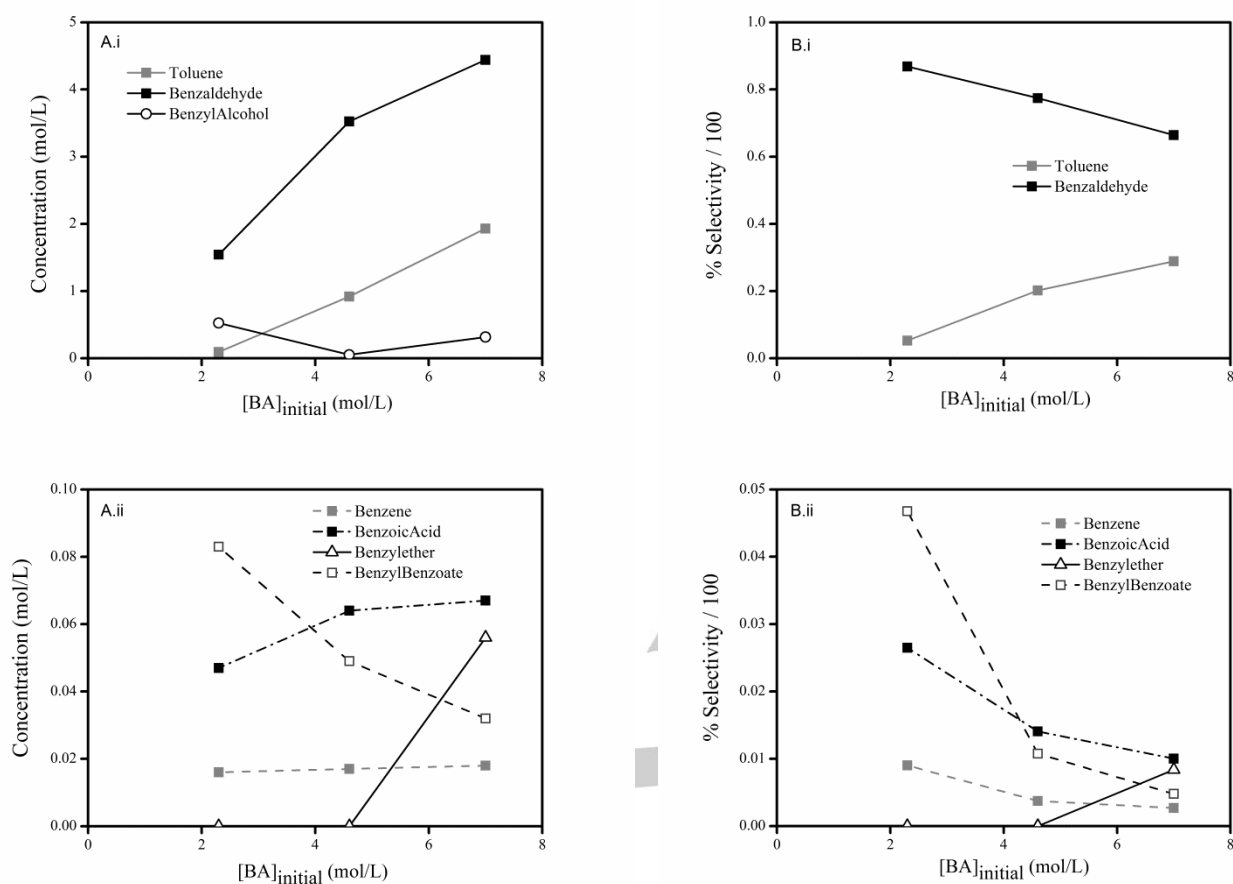
Alcohols can dissociate homolytically to produce an alkoxy intermediate: this reaction is known to occur on noble metal surfaces.<sup>[43]</sup> Previous surface science studies have shown that cleavage of an alcohol OH bond on noble metals is surface-oxygen assisted <sup>[28-29, 31, 38]</sup> (as has also been shown for water OH bond cleavage). We thus assume that alkoxy formation via a surface-oxygen assisted pathway -- to produce OH\* and Ar-CH<sub>2</sub>-O\* on the surface -- is the first step. We note that a recent computational study considered a surface hydroxyl to facilitate OH bond cleavage for ethanol on Au(111) and Pt(111),<sup>[44]</sup> and we cannot exclude such a mechanism here, so surface hydroxyl facilitated OH cleavage will be considered during microkinetic modeling.

Once an alkoxy is formed, aldehydes are often produced by hydrogen abstraction from the alkoxy intermediate on Pd and other noble metal surfaces.<sup>[34, 40]</sup> The literature suggests that hydrogen abstraction from alkoxy groups is not oxygen assisted and occurs with a Pd site abstracting the hydrogen directly.<sup>[29, 35, 37, 42]</sup> Additionally, a surface science study found that surface oxygen blocked abstraction of hydrogens from methoxy groups, again suggesting that empty Palladium sites are required.<sup>[40]</sup>

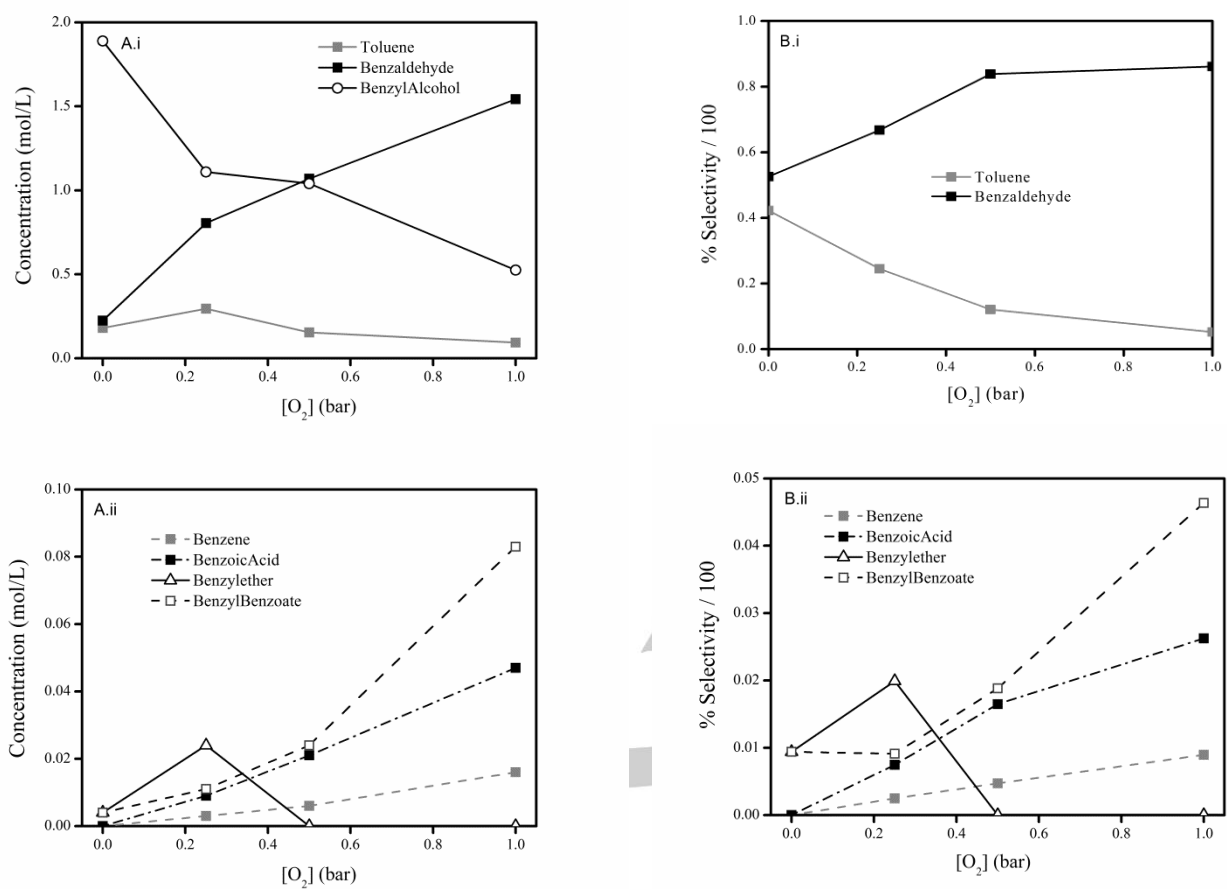


**Figure 1.** Typical kinetic profiles of A.i) major products and A.ii) minor products, shown for the conditions of experiment #2.

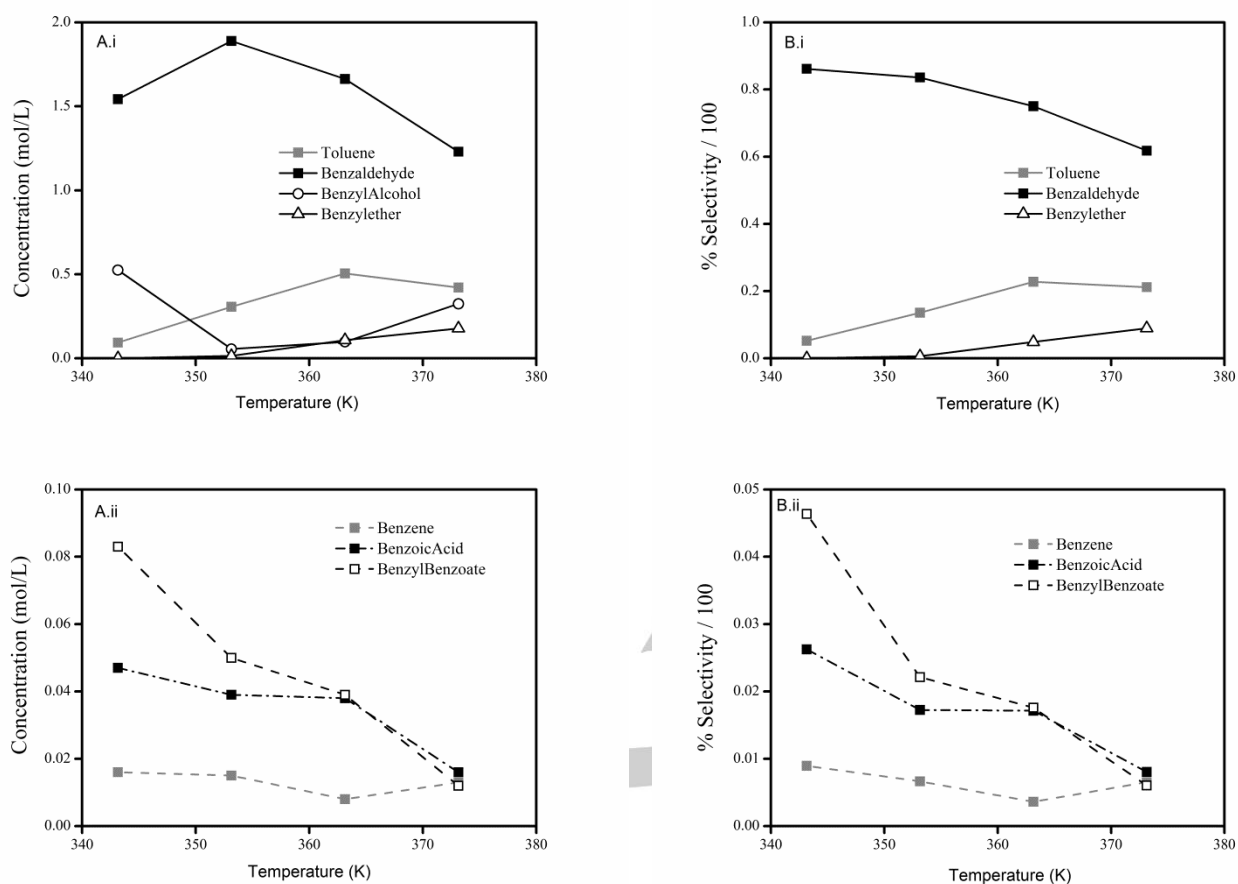
Thus, we assume that the aldehyde comes from the alkoxy intermediate and an adjacent open Pd site that abstracts a hydrogen directly, although it is also possible that a surface hydroxyl or surface oxygen abstracts the hydrogen.<sup>[44-45]</sup> Next, we note that the kinetic profiles of the aldehyde and toluene track for many of the experiments (see scaled plots of Exp. # 2, 3, 4, 6, 8, 9 in Supporting Information). From this observation, we infer that the toluene is produced from an alkyl group that originates from the same type of alkoxy intermediate as the aldehyde, but only as a minority product. This interpretation is consistent with literature data that methyl groups can be produced from methoxy groups on Palladium surfaces (analogous to the alkyl intermediate which leads to toluene), and almost never as more than a minority product.<sup>[30, 32, 35-36, 39]</sup> Density functional theory computations also show that the activation energy for direct dissociation to produce an alkyl group is much higher than the barrier to produce an alkoxy one.<sup>[46]</sup> We assume that C-H bond formation with the alkyl species occurs by addition of a hydrogen adsorbed directly on the surface, consistent with other studies.<sup>[25, 47-48]</sup> Temperature programmed desorption<sup>[49]</sup> of benzyl alcohol from neat Pd(111) produced toluene



**Figure 2.** Final concentrations (A.i and A.ii) and selectivities (B.i and B.ii) as a function of the initial alcohol concentration.



**Figure 3.** Final concentrations (A.i and A.ii) and selectivities (B.i and B.ii) as a function of the oxygen partial pressure in the gas flow.

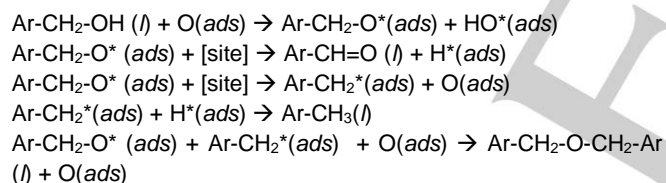


**Figure 4.** Final concentrations (A.i and A.ii) and selectivities (B.i and B.ii) as a function of the reactor temperature for each experiment.

while temperature programmed desorption<sup>[50]</sup> of benzaldehyde from neat Pd(111) did not produce toluene, indicating that the branching occurred prior to benzaldehyde formation, consistent with our interpretation. Temperature programmed desorption<sup>[49-50]</sup> of benzyl alcohol and benzaldehyde from oxygen pre-covered Pd(111) and vibrational spectroscopy<sup>[50]</sup> monitoring of the surface species is also consistent with our mechanistic assumption that an alkoxy intermediate is involved in benzaldehyde formation.

The ether molecule could be formed from combination of an alkyl group and an alkoxy group, or from two alkoxy groups with an oxygen left behind. In Figures 2-4 we see that the ether production displays similar trends to that of the toluene production as a function of initial concentrations and temperature (unlike benzene, benzoic acid, and benzyl benzoate). If we take toluene production to be proportional to alkyl formation, the correlated production suggests that the ether is formed from a combination of one alkoxy group with one alkyl group. A previous study found evidence that on Ag(110) diethyl ether was formed from a combination of one alkoxy group and one alkyl group,<sup>[41]</sup> but that a surface oxygen was likely also involved. At present, we will assume that a surface oxygen is also involved on Palladium, though confirmation would require additional study, and both options should be considered in future works. An alternative possibility provided by one of the reviewers is that the ether may be formed by nucleophilic attack of free benzyl alcohol on an adsorbed species.

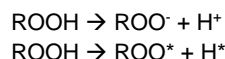
We can write the following equations based on the above analysis, where [site] represents a free active site such as a Palladium atom with no adsorbate:



These reactions are shown in the upper half of Scheme 1, and largely correspond to those of a recent publication on ethanol oxidation on Pd(111).<sup>[51]</sup> The pathways leading to benzyl aldehyde, toluene, and benzyl ether will be referred to as the "alkoxy route". We note that our proposed mechanism is consistent with the data that led to the hypothesis of a "disproportionation" mechanism.<sup>[19-21]</sup> In our proposed mechanism, toluene production is accompanied by formation of an additional surface oxygen while aldehyde production is accompanied by consumption of a surface oxygen (and formation of water precursors). This results in the same stoichiometry as a "disproportionation" reaction: 2 benzyl alcohol  $\rightarrow$  toluene + benzyl aldehyde + H<sub>2</sub>O. However, in Scheme 1, an alkyl intermediate is proposed to be involved for toluene formation, which is consistent with our data and mechanism for ether formation. Further study to resolve this issue is merited.

#### Carbonyloxy intermediate for benzene, benzoic acid, benzyl benzoate.

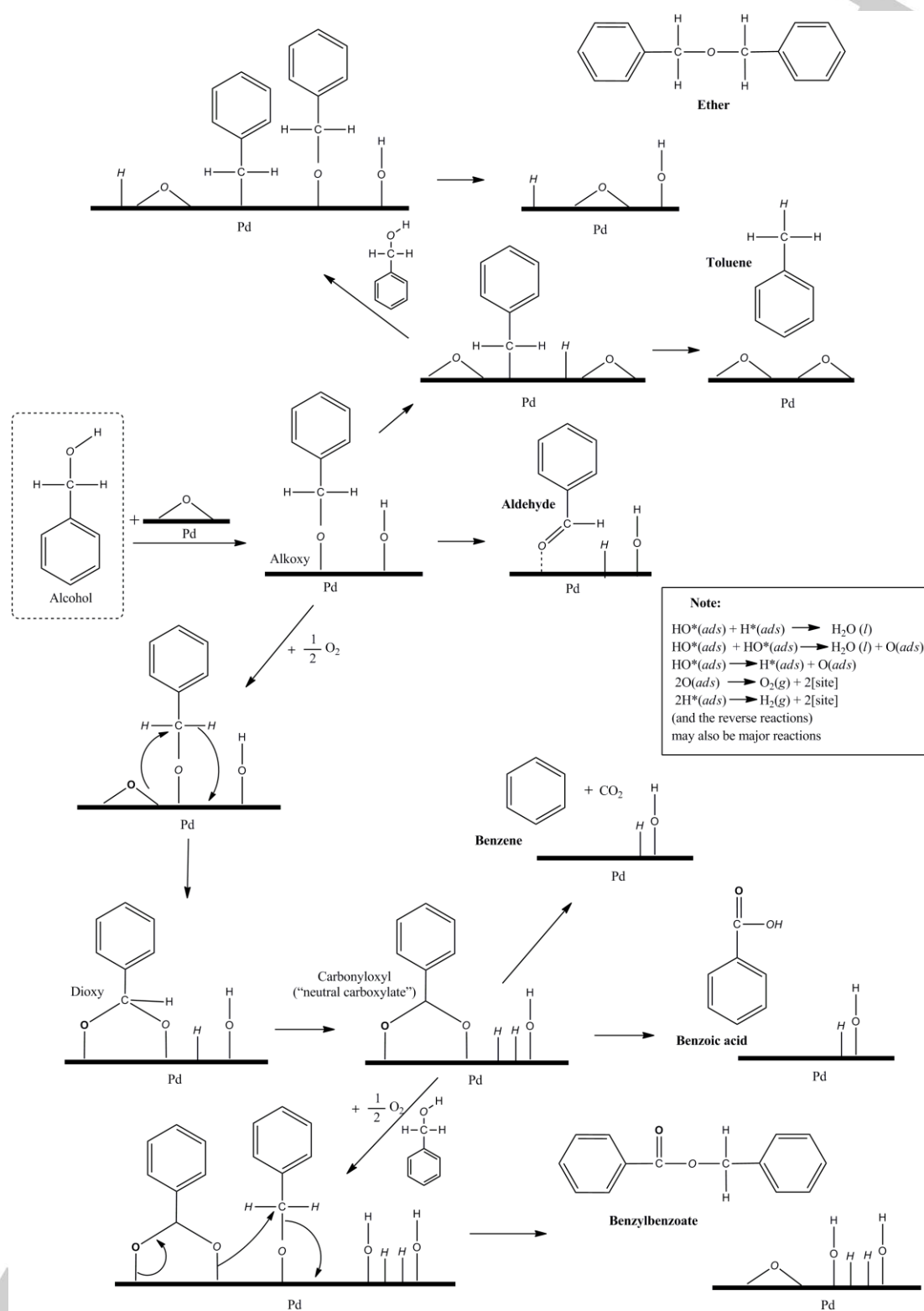
We make a nomenclature distinction between a carbonyloxy species and a carboxylate. This distinction is often neglected in the literature and can lead to confusion. The importance of this distinction can be demonstrated by comparing heterolytic vs homolytic cleavage of an organic acid:



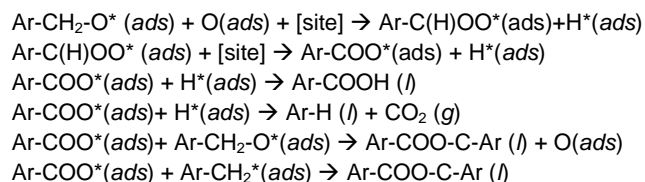
The heterolytic cleavage produces a carboxylate and a proton -- both are ionic species. In contrast, the homolytic cleavage produces a carbonyloxy radical<sup>[52]</sup> and a hydrogen radical. This distinction should be recognized when discussing the chemistry on surfaces. Carboxylates and protons (RCOO<sup>-</sup> and H<sup>+</sup>) are ionic species) are expected to be formed on many metal oxide surfaces.<sup>[53-54]</sup> In contrast, carbonyloxy and hydrogen atoms (RCOO<sup>\*</sup> and H<sup>\*</sup>) are neutral species which are expected to be formed on Palladium and other metal surfaces, in accordance with density functional theory.<sup>[55]</sup> Typically, transition metal surfaces cleave CH bonds and H<sub>2</sub> homolytically during adsorption,<sup>[56-58]</sup> in accordance with the Newns-Anderson model.<sup>[59]</sup> In line with the above distinctions, we will refer to Ar-COO<sup>\*</sup>(ads) as a **carbonyloxy** species, though we note that most of the literature cited uses words such as "carboxylate", "formate", "acetate," etc. when describing these types of carbonyloxy adsorbates on metals.

We start with the assumption that benzoic acid is formed from a dioxy or carbonyloxy intermediate. Next, we note that benzoic acid, benzene, and benzyl benzoate show similar kinetic profiles which track during many experiments (see scaled plots of Exp. # 1,2,3,6,8,9,10 in the supporting information) and that Figures 3-6 clearly show that the integrated production for benzene, benzoic acid, and benzyl benzoate display similar trends when varying the initial reactant concentrations and the temperature. These similar trends and kinetic profiles suggest a common intermediate, and in our mechanism we ascribe the role of a common intermediate to a carbonyloxy: if the carbonyloxy carbon of the carbonyloxy breaks off to form CO<sub>2</sub>, then benzene is the co-product. CO<sub>2</sub> has been observed as a co-product during benzyl alcohol oxidation,<sup>[10]</sup> and as a product alongside benzene production during temperature programmed desorption of benzyl alcohol on oxygen pre-covered Pd(111).<sup>[60]</sup> In general, reactions in which carbonyloxy decompose to form CO<sub>2</sub> and a hydrocarbon are known to occur over metals.<sup>[61-62]</sup> Experiments with ethanol are also consistent with our interpretation: Table 1 of reference<sup>[38]</sup> shows that CO<sub>2</sub> and ethanoic acid are produced after exposure of ethanol on Palladium at a common temperature during TPD, and the concomitant production of CO<sub>2</sub> and ethanoic acid was shown to occur from surface carbonyloxy.<sup>[31]</sup> From experimental data, it was determined that the route to form the acid product requires a surface hydrogen to react with a carbonyloxy.<sup>[31]</sup> The benzene product also requires a hydrogen source based on stoichiometry, and the similar concentration dependences suggest that the same hydrogen source is likely utilized, rather than the acid being formed directly by reaction of an alkoxy group with a hydroxyl group.<sup>[44]</sup> Additionally, the formation of benzyl benzoate

Scheme 1. Proposed mechanism for benzyl alcohol oxidation



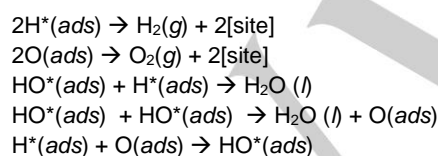
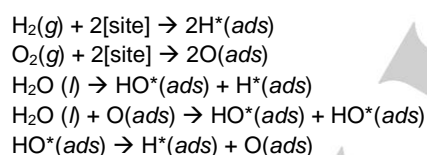
from a carbonyloxy species is a reasonable working hypothesis, though it is unclear whether the carbonyloxy reacts with an alkoxy group or an alkyl species (a question that microkinetic modeling may help with). The above analysis allows us to write the following equations:



These reactions are shown in the lower half of Scheme 1. The pathways leading to benzene, benzoic acid, and benzyl benzoate will be referred to as the "carbonyloxy/dioxy route". We have written the conversion of an alkoxy to a carbonyloxy as involving hydrogen abstraction by empty sites based upon literature evidence in the previous section, though it is also possible that a surface hydroxyl abstracts one or both of the hydrogen atoms involved.<sup>[44]</sup> We also note that an aldehyde decarbonylation route has previously been proposed for aliphatic aldehydes on Pd(111),<sup>[33]</sup> -- the corresponding reaction in our system would be benzaldehyde conversion to benzene, which we do not see evidence of. Perhaps steric hindrance or site blocking prevents aldehyde decarbonylation in our experiments. In several individual experiments (#s 2, 3, 9, 10) we see that aldehyde shows a long-term production that deviates from the long-term toluene production profile and resembles the carbonyloxy/dioxy route long-term production profile, so there may be a minor route of carbonyloxy converting back to aldehyde precursors, or the existence of multiple site types.

### Hydrogen, Oxygen, and Water Reactions

The following reactions are known to occur, and it is assumed that some gas phase molecules dissolve in the liquid phase prior to adsorption or after desorption.



### Lack of Product Readsorption

From the above considerations, we consider predicted and observed trends for the proposed reaction mechanism. With the exception of the starting alcohol, none of our observed species decrease across time, and no products that we observe are depleted. This suggests that none of the other species can displace the alkoxy or oxygen species on the surface, which

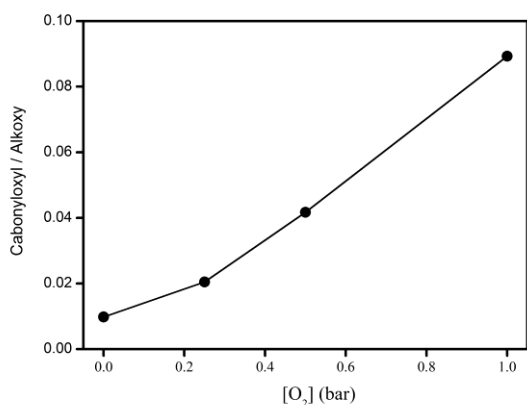
effectively prevents dissociative readsorption of the other products. In the context of our proposed mechanism, the lack of readsorption of products is not surprising: the surface is likely always covered with a combination of organics, oxygen, and hydrogen. All of the products would require 2 or more open sites to readsorb dissociatively, whereas the alcohol only requires one open site adjacent to a surface oxygen in order to dissociatively chemisorb. Thus, during the course of experiment the alcohol continues to dissociatively chemisorb while the products formed do not.

### Oxygen Pressure Dependence

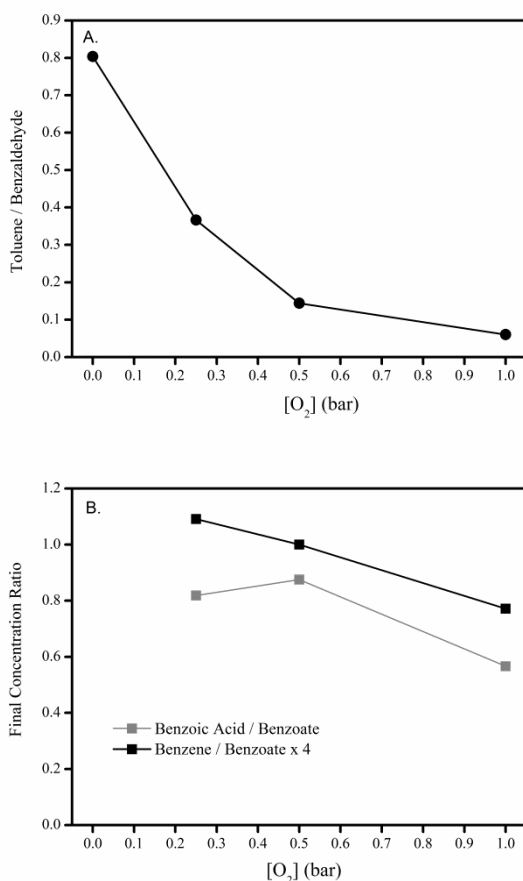
Figure 3 shows the oxygen pressure dependence of the integrated production for the species monitored. Several trends which are all consistent with our mechanism are observed. 1) Increased oxygen results in increased rate of reaction during the 120 minutes monitored and higher benzaldehyde production, consistent with the oxygen promoted alcohol dissociation mechanism 2) The benzoic acid, benzene, and benzyl benzoate integrated production increase as a function of oxygen, consistent with oxygen promotion of the carbonyloxy/dioxy route, by increased formation of carbonyloxy at the expense of alkoxy groups. The ratio of the carbonyloxy/dioxy route versus the alkoxy route shows this trend in Figure 5. 3) High oxygen pressures suppress formation of toluene and the ether, both of which require empty sites large enough for alkyl species, and both of which produce surface oxygen rather than consuming it.

In addition to promotion of alkoxide formation and site-blocking to prevent alkoxide dissociation,<sup>[29, 38, 40]</sup> oxygen plays important role by scavenging hydrogen atoms from the surface to form  $\text{OH}^*(\text{ads})$  and/or  $\text{H}_2\text{O}(\text{l})$ .<sup>[60-61]</sup> The consequence of this scavenging is that the selectivity of benzaldehyde vs. toluene and benzoic acid vs. benzoate should both decrease as a function of oxygen pressure, as both of those products require surface hydrogen as an intermediary reactant. There is literature evidence for acid formation suppression by oxygen,<sup>[31]</sup> and the expected trends are observed in Figures 6A and 6B. One topic of interest in the literature is why addition of Au to Pd nanoparticles increases selectivity to aldehydes.<sup>[63-64]</sup> Stabilities of the carbonyloxy and alkoxy may be an important factor.

The mechanism in Scheme 1 also explains the anaerobic oxidation of benzyl alcohol: as noted above, each toluene produced is accompanied by creation of an additional surface oxygen, while benzoate production and ether production result in no net production/consumption of surface oxygen -- whereas production of benzaldehyde, benzene, and benzoic acid all result in oxygen consumption. Thus, under anaerobic conditions the toluene route acts as a source of oxygen that the aldehyde route then consumes. Figure 3B.i and 6 show that in the absence of oxygen the toluene/benzaldehyde selectivity shifts towards the toluene route, and towards a 1:1 stoichiometry for toluene and aldehyde production.



**Figure 5.** The ratio of the carbonyloxy routes vs. the alkoxy routes increases with O<sub>2</sub> pressure, as determined based on final concentrations.



**Figure 6.** The ratio of the toluene production vs. benzaldehyde production, benzoic acid production vs. benzyl benzoate production, and benzene production vs. benzyl benzoate production. All are shown as a function of the O<sub>2</sub> gas flow partial pressure and are based on final concentrations.

### Initial Alcohol Concentration Dependence

Figure 2 shows the initial alcohol concentration dependence. We see several trends that are consistent with our mechanism. 1) Figures 2A.i and 2A.ii shows that the alkoxy route (aldehyde, toluene, benzyl ether) is promoted by additional alcohol 2) Figure 2B.ii shows that the selectivity towards the carbonyloxy/dioxy route is decreased as the alcohol concentration is increased, presumably because the surface is covered by more alkoxy groups leaving fewer opportunities for carbonyloxy/dioxy species to form. 3) The benzyl ether production shows a different initial alcohol concentration dependence relative to toluene or the aldehyde because the ether requires two adjacent aromatic groups (i.e., is 2<sup>nd</sup> order with respect to the alcohol).

In Figure 2A.i and 2A.ii, when changing initial concentration of alcohol, all products increase except for the benzoate, which decreases. The production of aldehyde indicates that alkoxy species are still being made, and the production of acid and benzene indicate that the carbonyloxy is still being made. However, the acid production increases by a quantity comparable to the benzoate decrease, so this phenomenon is probably due to increased surface hydrogen favoring the acid route. Figure 2B.i shows an increase in selectivity towards toluene rather than the aldehyde, supporting the interpretation that there is more surface hydrogen during the course of the experiment when the initial alcohol concentration is higher.

The ratio of the carbonyloxy route to the alkoxy routes show that with increasing initial alcohol concentration, the carbonyloxy routes are decreased relative to the alkoxy route. This is not surprising due to the competition between alkoxy groups and oxygen for surface sites, and similar mechanistic competition (carbonyloxy/dioxy route vs. alkoxy route) has been seen in experiments with Methanol on a PdO(101) thin film.<sup>[65]</sup>

### Temperature Dependence

In Figure 4, we see that the toluene and ether production increase as a function of temperature at the expense of the aldehyde production. The activation barrier for C-O breaking to form the alkyl intermediate from the alkoxy is likely higher than the barrier for aldehyde formation from the alkoxy (see earlier discussion, alkyl groups from C-O breaking in an alkoxy group on Pd surfaces are almost never formed as a major product). In this context, if the surface is covered, then the higher barrier route would be expected to become increasingly important at higher temperatures, as observed. There may also be a compounded effect if water production from surface oxygen increases as a function of temperature, such that the surface oxygen decreases leading to an increase in the toluene/ether route (similar to moving left in Figure 6A).

In Figure 4, we also see that the carbonyloxy/dioxy route decreases as a function of temperature. This trend is unlikely to be due to the activation barriers, since the activation barrier from alkoxy to carbonyloxy is probably larger than the barrier to the aldehyde, based upon the aldehyde appearing at lower temperature than the acid for TPD of ethanol on Pd(111).<sup>[31]</sup> Thus, we ascribe the trend of decreasing carbonyloxy/dioxy

route to a coverage effect, which we speculate as being due to decreased oxygen coverage during the course of experiment at higher temperatures.

With varying temperature, the final concentration of the alcohol (Figure 4A.i) suggests that at low and high temperatures adsorption of the alcohol is less favored. At low temperatures the alcohol absorption might be self-blocking due to a lower reaction rate, and at high temperatures the equilibrium for adsorption may be shifted towards fewer alkoxy groups on the surface.

### Remaining Questions

Several issues remain to be understood by future studies, likely to be resolved by microkinetic modeling and possibly density functional theory calculations.

- 1) Discrimination of whether the dominant mechanism for alkoxy formation from the alcohol is facilitated by a surface oxygen or instead a surface hydroxyl.
- 2) Elucidation of whether the ether molecule is formed from a) 2 alkoxy species, b) an alkoxy species and an alkyl species with a surface oxygen facilitating the reaction c) an alkoxy species and an alkyl species without a surface oxygen facilitating reaction.
- 3) Discrimination of whether abstraction of hydrogen from alkoxy groups occurs via empty sites or via a surface hydroxyl as the hydrogen acceptor (in the context of carbonyloxyl formation and separately in the context of benzaldehyde formation).
- 4) Discrimination between a molecular/alkoxy based disproportionation reaction versus an alkyl pathway for toluene formation.
- 5) Confirmation that some of the trends observed from varying the oxygen pressure are due to oxygen scavenging surface hydrogen.
- 6) Confirmation that the trends observed from varying temperature are partially due to decreased oxygen on the surface during the course of experiment.
- 7) It is currently believed that beta-hydrogen abstraction is the rate limiting step in aldehyde formation,<sup>[5]</sup> though with the complicated mechanism presented here there is likely more than one rate determining step, depending on the reaction conditions.

We are currently working towards a microkinetic modeling follow-up study with the aim of resolving several of the above issues.

### Conclusions

By using an experiment designed to keep the oxygen partial pressure constant in the gas phase, qualitative kinetic analysis of benzyl alcohol oxidation over carbon supported Pd nanoparticles has enabled us to elucidate the mechanism. The elucidated mechanism is shown in Scheme 1 and has the following main features: alkoxy intermediates are formed which

lead to benzaldehyde, benzyl ether, and toluene. The toluene and benzyl ether products share a common alkyl intermediate. A second route occurs when an alkoxy intermediate is converted to a carbonyloxyl ("neutral carboxylate"), and this pathway leads to benzene, benzoic acid, and benzyl benzoate. The proposed mechanism suggests that the selectivity is influenced by not only temperature and the coverage of the reactants, but also by the side reaction of oxygen scavenging surface hydrogen. Inclusion of the coverages of atomic hydrogen, atomic oxygen, and surface hydroxyls are expected to be required for a complete description of the quantitative kinetics.

## Experimental Section

### Materials

$\text{Na}_2\text{PdCl}_4$ , was from Aldrich (99.99% purity) and activated carbon from Camel (X40S; SA = 900–1100  $\text{m}^2/\text{g}$ ; PV = 1.5  $\text{mL/g}$ ; pH 9–10).  $\text{NaBH}_4$  of purity > 96% from Fluka, polyvinylalcohol (PVA) (Mw = 13000–23000 87–89% hydrolyzed) from Aldrich were used. Gaseous oxygen from SIAD was 99.99% pure.

### Catalyst preparation

Pd/AC (Palladium supported on activated carbon) was prepared following the procedure reported in ref.<sup>[6]</sup>. In brief,  $\text{Na}_2\text{PdCl}_4 \cdot 2\text{H}_2\text{O}$  (0.043 mmol) salt and freshly prepared 1 wt% PVA or PVP solution were added to 100 mL of  $\text{H}_2\text{O}$  (Pd/PVA ratio 1:1 wt/wt). After 3 min, a  $\text{NaBH}_4$  0.1 M solution (Pd: $\text{NaBH}_4$  mol ratio of 1:8) was added within few minutes from its generation, the suspension was acidified at pH 2 by sulfuric acid and the support was added under vigorous stirring. The catalyst was filtered and washed several times with distilled water. The samples were dried at 80 °C for 2 h. The amount of the support was calculated to obtain a final metal loading of 1 wt %. The particles have a size distribution from 2 to 8 nm, centered around 4 nm, and have been characterized by transmission electron microscopy.<sup>[16]</sup> The surface palladium comprises 31% of the total palladium atoms based on table 2.1 of ref.<sup>[66]</sup>, which is within 10% agreement of approximating the particles as spheres for most of the particles in the size distribution used here.

### Catalytic tests

Reactions were carried out in a 30 mL glass reactor equipped with a thermostat and an electronically controlled magnetic stirrer. 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 continuous flow of gas through the reactor such that the gas phase partial pressures remained constant during experiment (with the total pressure always 1 bar). Experiments used 60 mg of supported catalyst (0.6 mg of Palladium per sample). Benzyl alcohol and the catalyst were mixed in p-xylene. The benzyl alcohol/metal ratio was typically ~3000 mole alcohol / mole Pd. Various alcohol/xylene ratios were used during experiments (benzyl alcohol/xylene 25/75, 50/50 or 75/25 by percent volume) with the total liquid volume always kept at 10 mL. The reactor temperature was set to 70, 80, 90 or 100 °C and the oxygen flow set at 30 mL/min. Heating to the desired temperature was on the order of minutes, and reaction time zero was marked by the beginning of stirring. Periodic removal of samples from the reactor was performed via a syringe. Identification and analysis of the products was done by comparison with reference samples by gas chromatography

using a HP 7820A gas chromatograph equipped with a capillary column (HP-5 30m x 0.32mm, 0.25  $\mu$ m Film, made by Agilent Technologies) and a thermal conductivity detector. Quantification of reaction products was done by internal calibrations on the gas chromatograph using undecane as a standard. A stirring rate of 1250 rpm was used, and mass transfer effects were excluded by verifying that the same kinetic profiles were obtained with a stirring rate of 750 rpm for one experiment -- consistent with another study that found mass transfer was not rate limiting for stirring speeds of 500 rpm or above for a related catalyst system (supported AuPd nanoparticles) in a glass stirred reactor.<sup>[67]</sup> Based on mass balance of the aromatic rings (i.e., the concentration of aromatics at the end of experiment versus at the beginning of experiment), little to no organic evaporated during experiment (<10% of the reactants and products). Turnover frequencies were on the order of 1000 molecules per Palladium atom per hour (see supporting information), which is in line with literature results.<sup>[5, 68]</sup> Synthesis, experiments, and chemical analysis were performed at Università degli Studi di Milano. Data analysis and mechanistic analysis were performed primarily at Oak Ridge National Laboratory.

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**Keywords:** acetate • alkoxy • carbonyloxy • alcohols • palladium

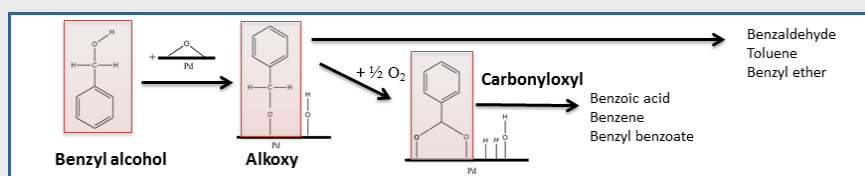
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**Title**

**Two key intermediates:** An alkoxy intermediate is proposed for benzyl aldehyde, toluene, and benzyl ether. A carbonyloxy intermediate is proposed for benzoic acid, benzene, benzyl benzoate.

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