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On the Role of Oxygen in the Liquid-Phase Aerobic Oxidation of Alcohols on Palladium

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The mechanism of alcohol oxidation was investigated using the conversion of cinnamyl alcohol (1) over Pd-based catalysts as a sensitive test reaction. Studies in a slurry reactor revealed that dehydrogenation and oxidative dehydrogenation of 1 follow the same reaction pathways independent of the presence or absence of oxygen and reaction conditions. Hydrogenation and hydrogenolysis side reactions indicated the presence of hydrogen on the metal surface during reactions. Catalyst deactivation in Ar is attributed to decarbonylation reactions and site blocking by CO. Introduction of molecular oxygen induced a dramatic enhancement of alcohol conversion rate by a factor of up to 285 due to oxidative removal of CO. Strong adsorption of CO on Pd/Al_2O_3 and its rapid removal by oxygen were corroborated by *in situ* ATR-IR spectroscopy. All these observations conform to a model according to which oxidation of 1 follows the classical dehydrogenation mechanism, and the key role of oxygen is the continuous oxidative removal of CO and other degradation products from the active sites. This oxidative cleaning of the metal surface allows a high rate of alcohol dehydrogenation even when the oxidation of the co-product hydrogen is slow and incomplete. It is likely that the observed effects are not limited to the oxidation of 1 on Pd, and regeneration of the active sites by oxygen generally plays an important role during aerobic oxidation of alcohols on platinum metals.

Key Words: **oxidation; dehydrogenation; palladium; cinnamyl alcohol; deactivation; decarbonylation; CO poisoning; ATR-IR spectroscopy.**

INTRODUCTION

Platinum-group metals (particularly Pt and Pd) and gold are active catalysts in the liquid-phase oxidation of alcohols, diols, and carbohydrates with molecular oxygen under close to ambient conditions (1–7). A dehydrogenation mechanism of the reaction is mostly accepted, assuming that the role of oxygen is to oxidize the co-product hydrogen formed in the rate-determining step and thus shift the equilibrium toward the carbonyl compound. The secondary importance of oxygen in this mechanism is supported by Wieland's early observation that the reaction can be carried out by replacing oxygen with a hydrogen acceptor such as quinone, nitrobenzene, or an olefin (8). This approach has been applied recently in the transfer dehydrogenation of allylic and aromatic alcohols on Pd using a cheap olefin as a hydrogen acceptor (9, 10).

In situ catalyst potential measurements provided further support to the dehydrogenation mechanism and to the secondary role of oxygen. Müller and Schwabe demonstrated for the first time that during oxidation of ethanol or 2-propanol the potential of Pt was in the "hydrogen region"; i.e., the metal was partially covered by hydrogen despite the presence of gaseous oxygen (11, 12). Some more examples of this situation can be found in the recent literature (13–15).

However, an increasing number of reports contradict this concept and suggest that oxidation of some alcohols proceeds on partially oxygen-covered metal surface and the actual concentration of adsorbed hydrogen during reaction seems to be negligible (16–20). These observations cannot easily be interpreted by the classical dehydrogenation mechanism. A feasible interpretation could be an oxidative dehydrogenation mechanism in which the adsorbed oxygen or OH species play a crucial role. The rate-determining elementary step might involve direct interaction of the adsorbed oxidizing species with the adsorbed reactant or its partially dehydrogenated intermediate (3, 7).

Several kinetic studies indicated a Langmuir–Hinshelwood-type behavior: a surface reaction between the adsorbed reactant and the dissociatively adsorbed oxygen in the rate-determining step (see, e.g., (21, 22)). In recent studies Markusse *et al.* suggested that oxygen-assisted dehydrogenation would be the rate-determining step (20, 23). However, kinetic analysis requires working under conditions free from mass-transport limitations, which conditions lead to a rapid catalyst deactivation due to "overoxidation" of the metal surface (24, 25)—an unpleasant obstacle in determining the real initial rate. It was also shown that multiple steady states may complicate the kinetic analysis (26, 27).

We can conclude that the apparent general agreement in the oxidative dehydrogenation mechanism of alcohol oxidation includes contradictory opinions concerning the

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real nature of elementary steps and the role of oxidizing species. Some years ago we proposed the blocking of active sites by strongly adsorbed alcohol degradation products as a possible explanation for this contradiction (18, 19, 28, 29). Oxidative removal of these impurities accelerates the target reaction; thus, adsorbed oxygen apparently plays an active (direct) role in the reaction mechanism.

This question is addressed here involving catalytic and *in situ* spectroscopic methods. The model reaction is the transformation of an allylic alcohol, *trans*-cinnamyl alcohol. Aerobic oxidation of allylic alcohols on Pt- and Pd-based catalysts under appropriate conditions affords sometimes excellent yields to α,β-unsaturated aldehydes (29, 30). In the absence of oxygen the selectivity is low due to side reactions in which the reactant alcohol acts as a hydrogen acceptor (10). The high reactivity of reactant and product offers the possibility to demonstrate the importance of competing side reactions, and to clarify the role of oxygen in these reaction pathways.

EXPERIMENTAL

Materials

The following commercial catalysts were used for alcohol oxidation: 5 wt% Pd/Al_2O_3 (Johnson Matthey 324; mean Pd particle size, 3.4 nm determined by TEM; calculated dispersion, 0.34 (31)), 5 wt% Pt/Al_2O_3 (Engelhard 4759; mean Pt particle size, 2.9 nm determined by TEM; calculated dispersion: 0.40), and 4 wt% Pd–1 wt% Pt–5 wt% Bi/C (Degussa, CEF 196 XRA/W). *trans*-Cinnamyl alcohol (Acros, 98%) was purified by recrystallization from petroleum ether (99.3% by ^1H NMR and GC). Ethylene glycol diacetate (Aldrich, 99+%, internal standard) and toluene (J. T. Baker, >99.5%) were used as received. Gases were of 99.999% purity (PANGAS).

Catalytic Studies

The reactions were performed in a 150-ml flat-bottomed glass reactor equipped with gas inlet, reflux condenser, thermometer, inlet for taking samples, and magnetic stirring. According to the general procedure, 0.10 g catalyst was prereduced *in situ* by H_2 for 10 min in 25 ml toluene, purged with N_2 for 5 min, and reoxidized by air for 30 min. The aim of this reduction–oxidation cycle was to activate the catalyst stored in air but to avoid the presence of any hydrogen when introducing the reactant. The catalyst prereduction temperature was lower by 20–25°C than the temperature of the alcohol oxidation reaction. After catalyst pretreatment the air flow was set in the range 5–60 ml min^{-1}, or the reactor was purged with argon and a balloon was filled when the reaction was carried out in an inert atmosphere. The reaction was started by injection of 1.0 g (7.5 mmol) cinnamyl alcohol and 1.1 g (7.5 mmol) internal standard in 5 ml toluene. Periodically withdrawn samples were analyzed by GC (Thermo Quest Trace 2000, equipped with an HP-FFAP capillary column and an FID). Products were identified by GC-MS and GC analysis of the corresponding authentic samples.

ATR-IR Spectroscopy

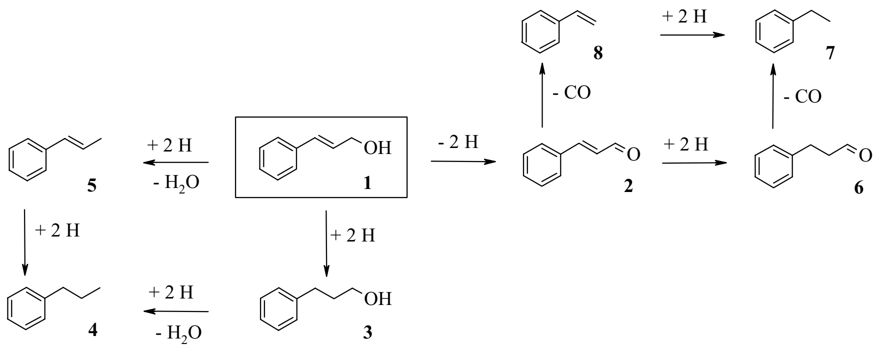
The transformation of cinnamyl alcohol (**1**) on Pd was studied by *in situ* attenuated total reflection (ATR) infrared spectroscopy (32). A catalyst layer on the internal reflection element was used for this purpose. A slurry of 10 mg 5 wt% Pd/Al_2O_3 in 5 ml toluene was stirred for 30 min. Then a ZnSe internal reflection element (IRE, 45°, $50 \times 20 \times 2$ mm, KOMLAS) was covered by dropping the slurry on its one side. The solvent was allowed to evaporate and the procedure was repeated three times. After drying for several hours in air the catalyst layer was ready for use. The catalyst exposed to the reaction mixture, a film of 3.1-cm^2 area, amounted to 1–1.5 mg.

ATR spectra were recorded using a home-built stainless-steel flowthrough cell with a total volume of 0.077 ml (33). The cell was heated to 60°C by a thermostat during the measurements. After assembling, the cell was mounted onto an ATR attachment (OPTISPEC) within the Fourier transform IR spectrometer (Bruker, IFS-66/S) equipped with an MCT detector. At the entrance and exit of the IRE the IR beam was collimated to minimize signal contributions from the O-ring region. Liquid (toluene or a toluenic solution of **1**) was flowed over the catalyst sample at a rate of 0.5 ml min^{-1} by a peristaltic pump (ISMATEC Reglo 100) located behind the cell. Liquid was provided from two separate glass bubble tanks where the liquids could be saturated with gases. The flow from the two tanks was controlled by a pneumatically activated three-way Teflon valve (PARKER PV-1-2324). After the sample compartment of the spectrometer was purged with dry air for about 1 h, neat toluene was admitted to the sample for 20 min. Then the catalyst was reduced *in situ* by admitting toluene saturated with H_2 for 10 min. After purging with Ar-saturated toluene for 10 min the catalyst was oxidized by flowing toluene saturated with air. Then the toluenic solution of cinnamyl alcohol was pumped over the pretreated catalyst and the spectra were recorded.

RESULTS

Reaction Network

Preliminary studies revealed a complex reaction network typical for the transformation of cinnamyl alcohol (**1**) to cinnamaldehyde (**2**) (Scheme 1). Changing the catalyst composition (Pd/Al_2O_3, Pt/Al_2O_3, and Pd–Pt–Bi/C), reaction atmosphere (Ar or air), solvent (toluene, cyclohexane, or water with detergent), and reaction temperature (45–80°C) had large influences on the relative contribution



SCHEME 1. Reaction network for the transformation of *trans*-cinnamyl alcohol (**1**) over alumina-supported Pd; all products were identified by GC and GC-MS.

of various reactions but the overall scheme was valid for all cases.

Besides the target reaction, dehydrogenation of **1** to **2**, a major reaction is the production of the saturated alcohol **3**. Formation of **3** may simply be interpreted as a transfer hydrogenation reaction in which the reactant itself plays the role of hydrogen acceptor. A similar reaction is the transformation of cinnamaldehyde (**2**) to dihydrocinnamaldehyde (**6**). We have shown recently (10) that many aromatic and allylic alcohols can act as hydrogen donors and acceptors on the Pd surface.

The appearance of 1-propenylbenzene (**5**) among the products is a clear indication of hydrogenolysis of the C–O bond in **1**. Further hydrogenation of the alkenyl side chain leads to propylbenzene (**4**), though this product may also form from **3** by C–O-bond hydrogenolysis.

Decarbonylation of cinnamaldehyde (**2**) affords styrene (**8**) and ethylbenzene (**7**) after hydrogenation. Alternatively, decarbonylation of dihydrocinnamaldehyde (**6**) also provides **7**. Note that Pt group metals, and particularly Pd, are good catalysts for aldehyde decarbonylation (34–36).

There was no indication of further oxidation of cinnamaldehyde to cinnamic acid in toluene. The likely explanation is that direct oxidation of the carbonyl group is slow and the faster dehydrogenation via hydration of the carbonyl group (the dominant mechanism in aqueous medium) is hampered by the stability of the aldehyde and the neutral apolar organic medium (29). Similarly, no C=C double-bond isomerization occurred, a reaction that is typical for aliphatic allylic alcohols, affording saturated aldehydes via enol-keto tautomerization (37–39). In cinnamyl alcohol the olefin function is in conjugation with the aromatic electron sextet; thus neither isomerization of cinnamyl alcohol into dihydrocinnamaldehyde nor isomerization of 1-propenylbenzene into allylbenzene took place.

In summary, formation of **3–7** indicates the presence of surface hydrogen during dehydrogenation or oxidation of cinnamyl alcohol, and the appearance of **7** and **8** verifies decarbonylation-type side reactions. This information is used in the next section to interpret the catalytic results.

Catalytic Dehydrogenation and Oxidation of Cinnamyl Alcohol

Dehydrogenation of cinnamyl alcohol in Ar over Pd/Al_2O_3 is characterized by a rapid loss of catalyst activity. An example is shown in Fig. 1. Before reaction the catalyst was activated by reduction with hydrogen and reoxidized in air to avoid the presence of surface hydrogen at the beginning of alcohol transformation. After addition of cinnamyl alcohol the first step is the reduction of the oxidized metal surface by the alcohol reactant. The initial rate of alcohol conversion related to the number of surface Pd atoms (TOF) was 450 h^{-1}. After 1 h the TOF was only 10 h^{-1} though the change in reactant concentration was minor. Apparently, conversion of cinnamyl alcohol is strongly poisoned on the reduced Pd surface. We propose that the loss of activity is due to aldehyde decarbonylation and the strong adsorption of CO, as shown in the following text.

After 90 min, Ar was replaced with air, which resulted in a dramatic rate acceleration (TOF 2850 h^{-1}) and conversion of the rest of the cinnamyl alcohol within 10 min. The

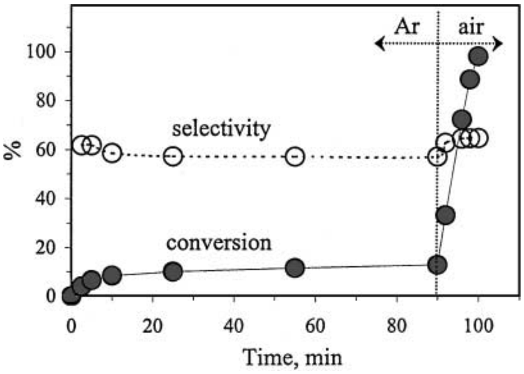


FIG. 1. Conversion of cinnamyl alcohol (**1**) and selectivity to cinnamaldehyde (**2**) in argon for 90 min and then in air. Conditions: 5 wt% Pd/Al_2O_3 prereduced by hydrogen and reoxidized by air *in situ* at 40°C; 1.0 g cinnamyl alcohol; 30 ml toluene; reaction temperature, 65°C; mixing frequency, 1250 min^{-1}; air flow rate, 60 ml min^{-1}.

TABLE 1

Product Distribution in the Transformation of *trans*-Cinnamyl Alcohol (1) over Pd/Al_2O_3[a]

				Yield (%)[b]							Selectivity (%)	
Entry	Atmosphere	Time (min)	Conv. (%)	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**2**	**3–7**
1a	Argon	90	10.7	5.7	4.1	0	0.5	0.1	<0.1	0.2	53	45
1b	Air	+25	99.8	62.8	34.9	0.2	0.5	0.6	0.8	<0.1	63	37
2	Air[c]	55	100	63.7	34.0	0.2	0.7	0.4	0.9	0.1	64	36
3	Air	85	24.7	21.9	1.5	<0.1	0.2	0.2	0.2	0.7	89	9

[a] Conditions: 0.10 g 5 wt% Pd/Al_2O_3 (prereduced by hydrogen and reoxidized by air *in situ* at 40°C); 1.0 g cinnamyl alcohol; 30 ml toluene; reaction temperature, 65°C; air flow rate, 20 ml min^{-1}; mixing frequency, 750 min^{-1}. For identification of the products see Scheme 1.

[b] No other products were detected by GC.

[c] The catalyst was prereduced before reaction with the reactant alcohol under N_2 atmosphere for about 3 min.

major products were cinnamaldehyde (**2**) and 3-phenyl-1-propanol (**3**). Interestingly, changes in selectivity with time and gas atmosphere were small (Fig. 1). The selectivity to **2** was higher by 5–7% on the oxidized Pd surface at the beginning of the reaction and after introduction of air.

The reaction was repeated at a lower rate of oxygen transport by reducing the mixing frequency and the air flow rate (Table 1, entry 1). The average TOF of alcohol conversion in air decreased from 2850 to 1150 h^{-1} but the product distribution barely changed. Note that in the second part of both reactions, in the aerobic oxidation, the rate-limiting step is the oxygen transport from the gas phase to the Pd surface, which is necessary to avoid too high oxygen coverage leading to catalyst "overoxidation" and deactivation (24, 25).

The product distribution before the introduction of air and at the end of the aerobic oxidation is shown in Table 1 (entries 1a and 1b). As discussed earlier, products **3–7**, formed by hydrogenation and hydrogenolysis reactions, evidence the presence of hydrogen on the Pd surface. Introduction of air after a 90-min reaction time disfavored the more demanding reaction, the hydrogenolysis of the C–O bond (to produce **4** and **5**) but barely hampered the saturation of the C=C bond (to produce **3**, **6**, and **7**). Similarly, oxygen only moderately retarded the decarbonylation of aldehydes **2** and **6** to the hydrocarbons **7** and **8**. A feasible explanation is that the amount of oxygen was sufficient to (partially) oxidize the impurities on the Pd surface but the surface oxygen concentration remained low and removal of hydrogen formed in the rapid dehydrogenation of **1** was incomplete.

The reaction in Table 1, entry 1, was repeated with only a 3-min period in Ar (Table 1, entry 2). The time required for complete conversion of **1** in air increased but the product distribution was very similar. The lower reaction rate is attributed to the incomplete reduction of the Pd surface by the reactant alcohol.

When the aerobic oxidation was started without any prereduction with the reactant alcohol in Ar, the conversion of **1** was even slower (entry 3). Note that the rate-enhancing effect of catalyst prereduction before the aerobic oxidation of alcohols on platinum-group metals is well known (40). More important is that the cumulative selectivity to hydrogenation and hydrogenolysis products **3–7** was 9%, demonstrating the presence of surface hydrogen on the partially oxidized Pd surface during aerobic oxidation.

These experiments indicate that the reaction rate and product distribution strongly depend on the amount of oxygen present on the Pd surface, but in all cases alcohol dehydrogenation (leading to partial hydrogen coverage) seems to be the dominant mechanism. On the basis of the product distribution shown in Table 1 we assume that the rapid deactivation of Pd/Al_2O_3 in Ar and the sharp rate enhancement by introduction of air are due to catalyst poisoning by the alcohol degradation product CO and to oxidative removal of these species, respectively. In the following we show more evidence for this concept.

The striking effects observed with Pd/Al_2O_3 could not be corroborated with Pt/Al_2O_3 due to its very low activity. For example, repeating the experiment shown in Fig. 1 with Pt/Al_2O_3 the TOF values were lower by up to three orders of magnitude. Thus, the differences due to variations in the catalyst pretreatment procedure could not reliably be measured. It has already been reported that Pt/Al_2O_3 is a poor catalyst for cinnamyl alcohol oxidation in aqueous alkaline medium (29).

Dehydrogenation and oxidation of cinnamyl alcohol on a Bi-promoted catalyst 4 wt% Pd–1 wt% Pt–5 wt% Bi/C provided further support for the presence of hydrogen on the metal surface during reaction (Table 2). The amount of products **3–7** formed by hydrogenation or hydrogenolysis-type reactions is considerable both in Ar and in air. The higher selectivity to cinnamaldehyde (**2**) in air (Table 2 and Fig. 2) is mainly attributed to suppression of transfer hydrogenation of cinnamyl alcohol. Decarbonylation affording **7** and **8** was barely detectable over Pd–Pt–Bi/C. The much lower decarbonylation activity of this three-component catalyst than of Pd/Al_2O_3 (last lines in Tables 1 and 2) is

TABLE 2

Product Distribution in the Transformation of *trans*-Cinnamyl Alcohol (1) over Pd–Pt–Bi/C[a]

			Yield (%)[b]							Selectivity (%)	
Entry	Atmosphere	Conv. (%)	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**2**	**3–7**
1	Argon	7.1	4.9	1.1	0.1	0.8	0.1	0	<0.1	69	30
2	Air	34.6	31.2	2.0	<0.1	1.0	0.2	<0.1	0.1	90	9.5

[a] Conditions: 0.10 g catalysts (prereduced by hydrogen and reoxidized by air *in situ* at 25°C); 1.0 g cinnamyl alcohol; 30 ml toluene; reaction temperature, 45°C; mixing frequency, 750 min^{-1}; air flow rate, 20 ml min^{-1}; reaction time, 5 h. For identification of the products see Scheme 1.

[b] No other products were detected by GC.

likely due to the promoting effect of Bi. It has been shown that Bi promotion can suppress CO formation during electrocatalytic oxidation of ethyleneglycol (41).

The reaction in air was considerably faster than that in Ar, as expected, but the sudden catalyst deactivation after a few minutes of dehydrogenation in Ar, as observed over Pd/Al_2O_3, was absent in the three-component catalyst (Fig. 2). We attribute this difference to suppression of side reactions that result in strongly adsorbing by-products or to weaker adsorption of these by-products on the Bi-promoted Pd surface. The contribution of Pt in the three-component catalyst seems to be negligible, based on the poor activity of Pt/Al_2O_3.

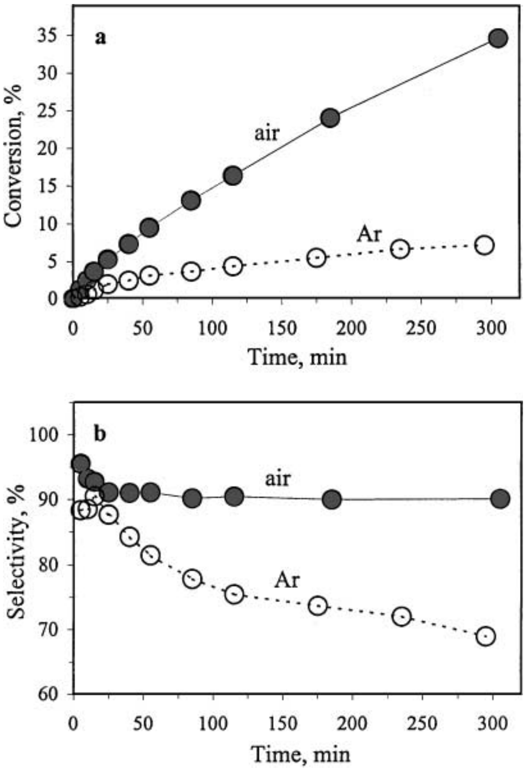


FIG. 2. (a) Conversion of cinnamyl alcohol (**1**) and (b) selectivity to cinnamaldehyde (**2**) in argon and in air over a Pd–Pt–Bi/C catalyst. Conditions: catalyst prereduced by hydrogen and reoxidized by air *in situ* at 25°C; 1.0 g cinnamyl alcohol; 30 ml toluene; reaction temperature, 45°C; mixing frequency, 750 min^{-1}; air flow rate, 20 ml min^{-1}.

ATR-IR Spectroscopy

The importance of decarbonylation reactions during dehydrogenation of cinnamyl alcohol has been investigated by ATR-IR of the solid–liquid interface. Figure 3 shows the *in situ* ATR spectra, which were recorded during flowing a solution of cinnamyl alcohol in toluene over the Pd/Al_2O_3 catalyst. The solution was first saturated with Ar (Fig. 3a), then with air (Fig. 3b), and subsequently with CO (0.5% in Ar, Fig. 3c). The bands in Fig. 3a at 2000, 1900, and 1840 cm^{-1} are attributed to adsorbed CO that forms during feeding the alcohol over the catalyst. The

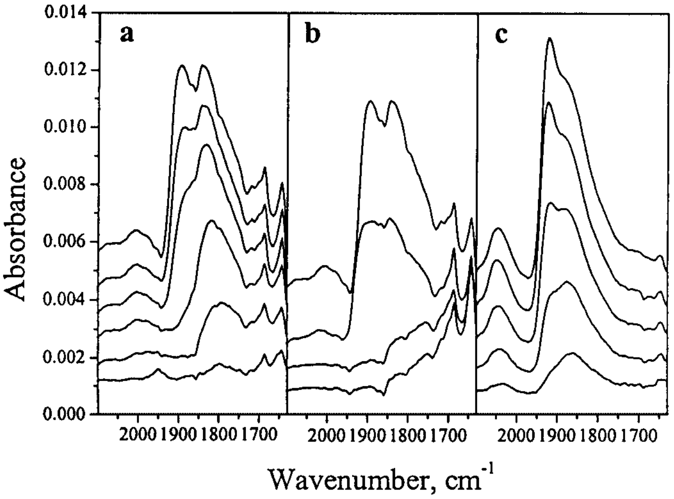


FIG. 3. (a) *In situ* ATR spectra recorded while flowing a solution of 0.056 mol/L cinnamyl alcohol in Ar-saturated toluene over Pd/Al_2O_3. The time lag between first (bottom) and last spectrum (top) is 17 min. (b) Spectra recorded while subsequently flowing an identical solution but saturated with air over the same sample. The time lag between first (top) and the last spectrum (bottom) is 2 min. (c) Spectra recorded while subsequently flowing dissolved CO (0.5% in Ar) in the same solution over the same catalyst. Time between first (bottom) and last (top) spectrum is 10 min. The background for the spectra shown in (a) and (b) was recorded before admitting the alcohol. For the spectra in (c) the background was recorded before admitting CO.

latter two bands are ascribed to bridged CO and the former one to linearly bound CO (42). The sharp bands at 1640 and 1690 cm^{-1} are associated with cinnamyl alcohol and species adsorbed on the Al_2O_3 support. It should be emphasized that the spectra were recorded truly *in situ*, that is, while the catalyst was working. GC analysis of the solution, which was passed through the cell, showed the production of cinnamaldehyde and 3-phenyl-1-propanol, the two major products over Pd, with yields over 0.5% for each. The spectra in Fig. 3a confirm that CO is built up on the alumina-supported Pd catalyst. The time difference between the first (bottom) and the last recorded spectrum (top) was 17 min.

Figure 3b reveals that CO formed during dehydrogenation of cinnamyl alcohol is rapidly removed when air is introduced into the system. The time difference between the first (top) and the last measured spectrum is about 2 min. For comparison, Fig. 3c shows the CO spectra obtained on the same catalyst when the reactant solution was saturated with CO. The relative intensity of the various CO bands and their behavior with coverage is qualitatively the same in Figs. 3a and 3c. For example, the low-wavenumber bridged CO band grows first, whereas the high-wavenumber CO band grows faster at higher coverage.

DISCUSSION

Oxidative Removal of Degradation Products

According to the classical dehydrogenation mechanism of alcohol oxidation over platinum-group metals, the rate-limiting step is dehydrogenation on the metal surface and the role of oxygen is to oxidize the co-product hydrogen to water, thereby accelerating the overall reaction. Dehydrogenation and oxidative dehydrogenation of primary unsaturated alcohols, such as cinnamyl alcohol, are a sensitive test reaction for studying the reaction mechanism and the role of oxygen in the aerobic oxidation of alcohols. The catalytic studies, presented in Tables 1 and 2 and Figs. 1 and 2, revealed that transformation of cinnamyl alcohol runs over the same reaction pathways independent of the presence or absence of molecular oxygen, reaction conditions, and catalyst composition. Formation of by-products **3–7** (Scheme 1) demonstrated that there was always a sufficient amount of hydrogen on the metal surface to allow hydrogenation and hydrogenolysis side reactions. Hence, these results prove that the classical dehydrogenation mechanism is valid for the oxidation of cinnamyl alcohol on Pd.

Formation of **3–7** via hydrogenation and hydrogenolysis of reactant and products even in the presence of molecular oxygen indicates that oxidation of the co-product hydrogen by oxygen on the Pd surface is unexpectedly slow. The experiments in Fig. 1 and Table 1, entry 1, demonstrate that dehydrogenation of **1** can be accelerated by more than two orders of magnitude by introducing oxygen and without significantly hampering the side reactions involving surface hydrogen. These observations question the validity of the general assumption that the role of oxygen would be oxidation of the co-product hydrogen, and thus regenerating free active sites and accelerating the overall reaction.

The present study corroborates our former proposal (18, 19, 28, 29) that in many liquid-phase alcohol oxidation reactions the major role of oxygen is the oxidative removal of degradation products. The dramatic rate acceleration achieved by introducing oxygen (Fig. 1) is not an indication of a direct involvement of adsorbed oxidizing species in the alcohol dehydrogenation mechanism but is rather due to removal of strongly adsorbed species and an increase in the number of active Pd^0 sites available for alcohol dehydrogenation. Decarbonylation of cinnamaldehyde (**2**) and dihydrocinnamaldehyde (**6**) affords CO and hydrocarbons (styrene (**8**) and ethylbenzene (**7**), respectively, Scheme 1). Introduction of molecular oxygen suppressed but did not eliminate this side reaction (Tables 1 and 2). *In situ* ATR-IR spectroscopy revealed a considerable CO coverage on the Pd surface during dehydrogenation of cinnamyl alcohol in Ar and proved the subsequent oxidative removal of CO by introducing air (Fig. 3).

Pd is one of the best decarbonylation catalysts (34–36, 43). That is, the transformations **2** → **8** and **6** → **7** in Scheme 1 are not only fast but also selective. The produced hydrocarbons and CO_2 (after oxidation of CO) can easily desorb from the metal surface and thus regenerate the active sites. However, in other reactions and on other metals, oxidative removal of CO may not be sufficient to regenerate the alcohol dehydrogenation activity. In general, a decarbonylation reaction produces CO, hydrogen, and C_{n-1} hydrocarbon species, as shown by Barteau and coworkers under UHV conditions (35, 36). In addition to CO, the hydrocarbon fragments formed in the decarbonylation reaction can cause catalyst poisoning. We have reported recently that alcohol dehydrogenation may be accelerated but also retarded by addition of an olefin as hydrogen acceptor (10). For example, styrene reduced the rate of dehydrogenation of 1-phenylethanol to acetophenone on Pd/Al_2O_3 by a factor of more than 30, compared to the reaction in Ar without olefin. Note that styrene is the decarbonylation product from cinnamaldehyde (**8** in Scheme 1).

Electrocatalytic studies of the adsorption and reactions of allyl alcohol on Pt and Pd indicated that removal of strongly adsorbed hydrocarbon fragments (decarbonylation products) as easily desorbing hydrocarbons requires strongly reducing conditions (44, 45). It was also reported that the best regeneration process for a catalyst deactivated in alcohol oxidation is a high-temperature treatment in hydrogen (46). Hence, we assume that the observed low activity of Pt/Al_2O_3 in cinnamyl alcohol dehydrogenation may be due to catalyst poisoning by strongly adsorbed hydrocarbon species and by the possible oligomerization products. This assumption explains the minor positive effect of oxygen on the dehydrogenation rate. Apparently, in this reaction Pd is less sensitive to poisoning by the hydrocarbon fragments.

A possible alternative explanation to the positive effect of oxygen introduction during dehydrogenation of **1** would be that in air the Pd surface is partially covered by oxygen. Partial coverage of the active sites by oxygen can, for example, reduce the size of active site ensembles and thus suppress side reactions, and shift the catalyst potential leading to different adsorption strength and reaction rates. To estimate the contribution of oxygen-covered metal surface to the overall performance of the catalyst we have to keep in mind that the reduced metallic sites are more active than the oxidized sites by at least an order of magnitude (40). During our experiments the selectivity to products formed by hydrogenation and hydrogenolysis was in the range 9–37% even in the presence of air (Tables 1 and 2). This is an indication that the major part of the Pd surface was in a reduced state and partially covered by hydrogen. Hence, the key role of oxygen is assumed to be the oxidative removal of degradation products.

Generalization of the Observations

The role of oxygen in the aerobic oxidation of alcohols can be illustrated by the bell-shaped curve in Fig. 4. It was early discovered that the oxidized metal (region a) is poorly active in alcohol oxidation (40). Prereduction of the supported metal catalyst by hydrogen, or by the reactant itself in an inert atmosphere, can accelerate the reaction dramatically (moving from right to left on the curve in Fig. 4). The present results, and also former observations (18, 19, 28, 29), indicate that below a certain oxygen coverage of the metal (region b) the rate decreases again due to catalyst poisoning (region c). An important role of oxygen is to remove the poisoning species and thus increase the number of active M^0 sites available for alcohol dehydrogenation. During development of an alcohol oxidation process, the aim is to operate the reactor at around region b by fine-tuning the rate of oxygen supply to the actual rate of alcohol oxidation.

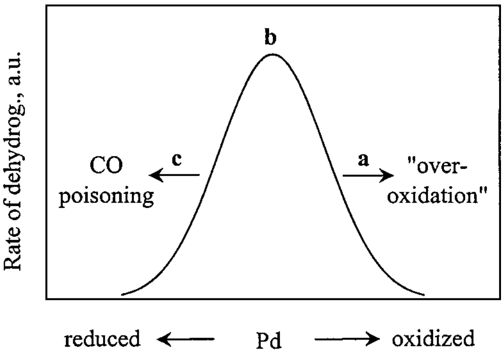


FIG. 4. Schematic representation of the rate of alcohol dehydrogenation as a function of the oxidation state of Pd.

Catalyst deactivation during aerobic oxidation of alcohols is commonly interpreted as overoxidation of the metal catalyst. On the basis of Fig. 4 the distinction between catalyst poisoning by surface impurities and deactivation due to too-high oxygen coverage (overoxidation) is simple. An unambiguous test is to follow the reaction rate as a function of the oxidation state (potential) of the catalyst (15). *In situ* catalyst potential measurements revealed that during oxidation of L-sorbose the reaction rate was negligible on a reduced, partially H-covered Pt surface (19). By increasing the rate of oxygen supply (i.e., moving from left to right on the bell-shaped curve in Fig. 4), the rate of sorbose conversion reached a maximum corresponding to a relatively clean surface and moderate oxygen coverage, then decreased again due to too-high oxygen coverage of Pt.

Another important question is the scope of reactants prone to decarbonylate on Pt or Pd. We propose that catalyst poisoning by alcohol degradation should be expected in all reactions where the product is an aliphatic (35, 36) or aromatic aldehyde (47), or an activated ketone (43) (for example, an α-ketoacid, a typical oxidation product in carbohydrate oxidation). There is substantial literature on the facile decarbonylation, or more generally on the degradation, of carbonyl compounds on platinum-group metals affording CO and a hydrocarbon residue (34–36, 43, 47, 48). Unexpectedly, even the dehydrogenation of simple secondary aliphatic alcohols, such as 2-propanol, on Pt (49) and Pd (50) may be accompanied by degradation to CO and hydrocarbon fragments. For example, exposure of Pd(110) to 2-propanol at 120 K leads to the formation of CO, CH_4, hydrogen, and surface carbon (50). Hence, poisoning of platinum-group metals by CO and hydrocarbon fragments seems to be a general phenomenon during dehydrogenation and oxidative dehydrogenation of alcohols.

Finally, we have to emphasize an interesting consequence of reactant and product degradation and the positive effect of oxygen on the reaction rate. A positive order of oxygen concentration on the alcohol oxidation rate is frequently used to support a reaction mechanism in which adsorbed oxygen is directly involved. However, this conclusion is acceptable only when retardation by degradation products and their oxidative removal can be excluded.

CONCLUSIONS

Dehydrogenation and oxidative dehydrogenation of cinnamyl alcohol over Pd-based catalysts and *in situ* ATR-IR spectroscopic analysis of adsorbed species on Pd/Al_2O_3 under reaction conditions indicate the following mechanistic model:

1. The reaction obeys the classical dehydrogenation mechanism in which adsorbed oxidizing species do not play a role.

2. Contrary to the general assumption, oxidation of the co-product hydrogen by oxygen is not a necessary requirement for achieving high reaction rates.
3. The major role of oxygen is the oxidation of strongly adsorbed CO produced by decarbonylation-type side reactions. Continuous oxidative removal of CO ensures a high number of free Pd^0 sites available for the dehydrogenation reaction.
4. The C_{n-1} hydrocarbon fragments (co-products of the decarbonylation reactions), or the dimers and oligomers formed from them on the metal surface, can also lead to catalyst deactivation. Removal of these species by oxygen is inefficient.

We propose that this model can be applied to many other alcohol oxidation reactions over platinum-group metal catalysts. The large differences observed in the reactivity of various metal catalysts may partly be due to the different extent of catalyst poisoning by degradation products and to the efficiency of oxygen to regenerate the active sites. The contradictory observations concerning the role of oxygen in the reaction mechanism may be explained by the dramatic effect of oxidative removal of strongly adsorbed degradation products on the reaction rate. A positive order to oxygen in the kinetic analysis does not necessarily indicate a Langmuir–Hinshelwood mechanism with direct involvement of oxygen. An unambiguous interpretation of the role of oxidizing species requires *in situ* investigation of the surface species and the role of the oxidation state of the catalytic metal surface.

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