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# Liquid-Phase Oxidation of 2-Propanol to Acetone by Dioxygen Using Supported Platinum Catalysts[1a]

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Platinum supported on silica, carbon, and alumina catalyzes the oxidation in water of 2-propanol to acetone by dioxygen. The kinetics of the oxidations fit two different patterns, depending on conditions: one in which the reaction rate is determined by the rate of transport of dioxygen to the catalyst surface, and one in which the rate is set by a reaction occurring on the catalyst surface (probably cleavage of the secondary C–H bond of 2-propanol). The most effective catalysts for this oxidation are those having intermediate values of dispersion $D$ (the fraction of platinum atoms present on the platinum surface): $D \simeq 10\%$. Platinum on silica is a more active catalyst than platinum on carbon or alumina, for the same values of dispersion of platinum. The lifetime of the catalyst is relatively short, and conversion of 2-propanol to acetone incomplete. The lifetime and activity are limited by at least three processes: irreversible oxidation of platinum to platinum oxide by dioxygen; weak adsorption of acetone on the catalyst surface in competition with adsorption of 2-propanol; strong adsorption on the catalyst surface of minor impurity products of unknown structure (possibly carboxylic acids). The oxidation of catalytically active platinum(0) to catalytically inactive platinum oxides by dioxygen is more rapid for small platinum particles than for large ones and more rapid in water than in air. The activity of deactivated catalyst can be partially regenerated by washing and treating with $H_2$ at 1 atm and 27 °C and completely regenerated by washing and treating with $H_2$ at 1 atm and 230 °C. Quinones and olefins do not substitute for dioxygen as hydrogen acceptors in this oxidation; oxidized methylene blue does substitute, but rates are slow; hydrogen peroxide is an effective oxidant, but the interpretation of results using it are complicated by its rapid disproportionation to $O_2$ and $H_2O$ catalyzed by platinum. The Arrhenius activation energy for oxidation of 2-propanol over the Pt/C catalyst is $E_a = 9.1 \pm 0.2$ kcal/mol, in the non-mass-transport limited kinetic regime.

## Introduction

A variety of techniques are available for the selective oxidation of hydroxyl groups in carbohydrates and alcohols.[2-30] Among these, catalytic oxidation by dioxygen catalyzed by platinum or palladium is one of the most attractive.[4-32] If the hydroxyl group is primary, the reaction produces aldehydes in neutral or acidic solutions and carboxylic acids in basic solutions. Secondary alcohols yield ketones (eq 1 and 2). The reaction proceeds under

$$RCH_2OH \xrightarrow[\text{Pt or Pd}]{O_2} RCHO + RCO_2H + H_2O \qquad (1)$$

$$R_2CHOH \xrightarrow[\text{Pt or Pd}]{O_2} R_2C{=}O + H_2O \qquad (2)$$

mild conditions: aqueous solutions, low (>1–2 atm) pressures of dioxygen, and moderate (25–80 °C) temperatures.[6-9] Water is the most common solvent, but organic solvents can be used.[8,9] For hydrophobic solvents, the reaction must be run at low (<10%) concentrations of alcohol to avoid clumping of the catalyst by the water produced.

The most attractive feature of this system is that it is capable of oxidizing a single hydroxyl group selectively in many polyhydroxylic molecules, as illustrated by oxidations of pentaerytritol to the corresponding monocarboxylic acid,[4] *myo*-inositol to *myo*-inosose,[7] methyl α-D-glucopyranoside to α-D-glucopyranosiduronic acid,[8] L-sorbose to 2-keto-L-gulonic acid,[11] and D-glucose to D-gluconic acid.[31]

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The primary reason that this reaction is not more widely used is that, as commonly run, it requires a high ratio of catalyst to substrate. For laboratory-scale preparations, the amount of platinum (supported or unsupported) commonly used is 10–20% by weight of the compound to be oxidized.[6-9] This large amount of catalyst is necessary because it deactivates during the reaction. Catalyst lifetimes are much longer in industrial application.[30]

A major objective of this study is to establish the process leading to catalyst deactivation and to explore reaction conditions that extend the catalyst lifetime or permit regeneration of the catalyst. It involves highly dispersed, supported metal catalysts of the type used in synthetic applications. An accompanying, complementary mechanistic paper uses electrochemical and stereochemical probes to provide alternative views of the processes occurring at the catalyst surface.[22]

Platinum in the form of reduced platinum oxide (Adam's catalyst) or platinum on carbon (Pt/C) is the most commonly used metal for these catalytic oxidations. Palladium has also been used[8,9,32] but is less stable to oxidation.[20] Many other metals oxidize alcohols catalytically at high temperature in the vapor phase.[32-40] Relevant studies have also examined the mechanism of the following: alcohol dehydrogenation in the absence of oxygen using nickel,[39,41] copper,[42] platinum,[41,43,44] ruthenium,[43] palladium,[41] iron,[41] and rhodium[45] catalysts; the gas-phase adsorption of alcohols, aldehydes, ketones, and carboxylic acids on several metals;[35,36,46-57] the adsorption from solution and electrooxidation of alcohols, aldehydes, ketones, and carboxylic acids at metal electrodes.[57-68]

Previous studies of the platinum- and palladium-catalyzed oxidation of alcohols have generated two major mechanistic hypotheses: that the reaction is a dehydrogenation of the alcohol at the surface of the metal catalyst, and that the reaction requires reaction of the alcohol with dioxygen or some derived species on the catalyst surface. The observation that oxidized methylene blue or quinone can be used as oxidant in place of dioxygen,[22,69] plus electrochemical,[22,70] stereochemical,[23] and isotopic labeling studies argue for dehydrogenation of the alcohol, and more specifically cleavage of the $\alpha$-C–H bond, as the critical step.

Jaffe and Pleven studied the oxidation of di-*O*-isopropylidene-L-sorbose to the corresponding 2-keto-L-gulonic acid in some detail.[20,30] They reported the following: palladium was less reactive and more easily poisoned than platinum; the reaction initially showed zero-order kinetics in substrate; the catalyst lifetime was extended by running the reactions at low oxygen partial pressures; limited quantities of the product could be generated by treatment of the substrate with Pd/C in the absence of dioxygen. Schwartz et al.[26] examined the gas-phase oxidation of a variety of organic compounds on platinum and palladium and concluded that the oxidation of 2-propanol proceeded through an initial cleavage of the $\alpha$-C–H bond. These results are consistent with a dehydrogenation mechanism and conflict with the proposals that adsorbed oxygen is necessary for reaction to occur. Alternative mechanistic proposals involving reaction of alcohol with oxygen-containing surface species (adsorbed dioxygen or oxygen; platinum or palladium oxides) as the critical step have also been seriously pursued.[12-14,18,19]

## Results

We chose to study the oxidation of 2-propanol to acetone for several reasons. Both 2-propanol and acetone are completely soluble in water and organic solvents, stable under the reaction conditions, and easily analyzed by gas–liquid permeation chromatography (glpc). Within the limits of our analytical techniques, oxidation of 2-propanol generated only acetone as product (although minor products were almost certainly formed in quantities sufficient to influence activity of the catalyst (see below)).

The catalysts used were platinum supported on carbon, silica, or alumina. Most reactions were variants on a standard set of concentrations and conditions: 100–400 mg of catalyst containing 1–10% w/w platinum; a 0.20 M solution of 2-propanol in unbuffered water; $P_{O_2}$ = 1.34 atm (5 psig). The oxidations were conducted in a 100-mL round-bottomed flask with rapid magnetic stirring. In the determination of the behavior of the catalyst, water and 2-propanol were normally mixed first, and the dioxygen was then introduced.

*Preparation and Characterization of Catalysts.* We prepared catalysts by reduction of $(COD)Pt(CH_3)_2$ (COD = 1,5-cyclooctadiene), $K_2PtCl_4$, or $H_2PtCl_6$ with dihydrogen. The catalysts were not pyrophoric and could be stored in contact with air without loss in activity. The dispersion (%*D*, eq 3; the ratio of surface

$$\%D = 100\frac{Pt_s}{Pt_T} \quad (3)$$

platinum atoms ($Pt_s$) to total platinum in the sample space ($Pt_T$)) of the catalyst was measured by titration with dihydrogen and dioxygen using standard procedures.[71]

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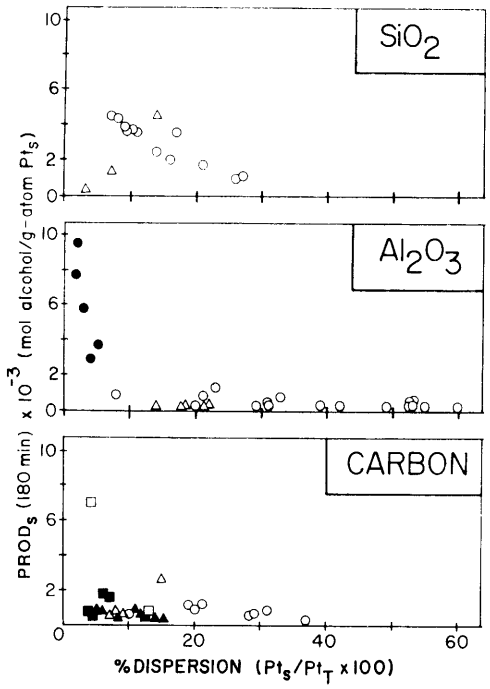


**Figure 1.** $PROD_s$ (180 min) vs percent dispersion: 1.34 atm of $O_2$, $[P]_0$ = 0.20 M. Complexes used to prepare catalysts: ○ $(COD)PtMe_2$ (dry); ● $(COD)PtMe_2$ (calcined); △ $H_2PtCl_6$ (dry); ▲ $H_2PtCl_6$ (wet); □ $K_2PtCl_4$ (dry); ■ $K_2PtCl_4$ (wet).

The turnover number (TN) is a measure of the catalytic activity of the surface platinum in the sample. The TN is calculated as the number of substrate molecules that react per surface platinum atom per minute:

$$TN_s = \frac{\text{mol of alcohol reacted}}{\text{mol of Pt}_s \times \text{time (min)}} \quad (4)$$

The subscript "s" indicates that the TN is calculated on the basis of *surface* platinum atoms. During all of these oxidations of 2-propanol, the catalyst deactivated during the reaction and the instantaneous TN decreased with time. To designate the *total* quantity of product formed by the catalyst during these reactions (usually 180 min), we use the productivity ($PROD_s$ or $PROD_T$):

$$PROD_s \text{ (time } t) = \frac{\text{mol of alcohol reacted (in time } t)}{\text{mol of Pt}_s} \quad (5)$$

$$PROD_T \text{ (time } t) = \frac{\text{mol of alcohol reacted in time } t}{\text{mol of Pt}_T} \quad (6)$$

In almost every experiment, the catalyst was completely deactivated by the end of this reaction period, and the productivity (180 min) was a measure of the integrated conversion over the entire active catalyst lifetime. Figure 1 shows plots of the $PROD_s$ as a function of platinum dispersion for different catalysts. These catalysts display a wide range of activities, and although there is a general trend in increasing $PROD_s$ with decreasing dispersion, even catalysts with the same dispersion could show different activities if prepared under different conditions.

Figure 1 indicates that different methods of preparation influence catalyst activity. The use of $(COD)PtMe_2$ as the platinum source gave the greatest range of dispersions and highest activities. For this reason and because $(COD)PtMe_2$ introduces no halide ion contamination into the system, $(COD)PtMe_2$ was the precursor for most of our catalyst preparations. The support also influenced the properties of the catalysts. Alumina produced a wide range

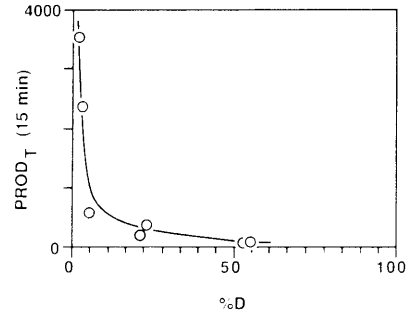


**Figure 2.** Initial activities for several $Pt/Al_2O_3$ catalysts with different dispersions: 1.34 atm of $O_2$, $[2\text{-propanol}]_0$ = 0.20 M.

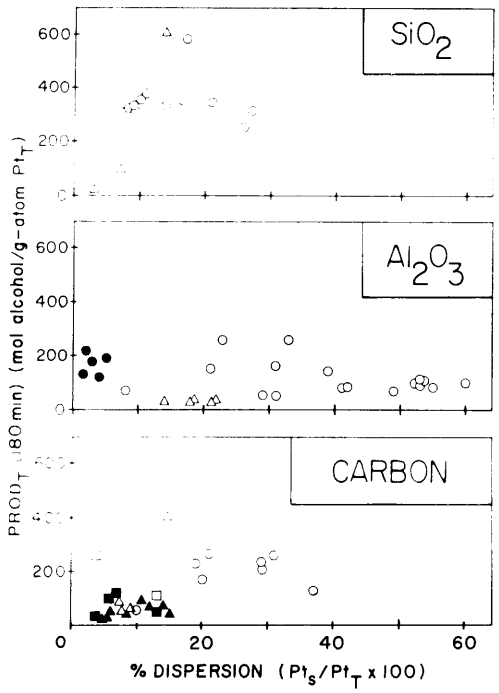


**Figure 3.** $PROD_T$ (180 min) vs percent dispersion: 1.34 atm of $O_2$, [P] = 0.20 M. Complexes used to prepare catalysts: ○ $(COD)PtMe_2$ (dry); ● $(COD)PtMe_2$ (calcined); △ $H_2PtCl_6$ (dry); ▲ $H_2PtCl_6$ (wet); □ $K_2PtCl_4$ (dry); ■ $K_2PtCl_4$ (wet).

of dispersions but gave catalysts with lower activity. The carbon-supported catalysts generally showed low dispersion and low activity. Platinum supported on silica gel was the most active class of catalyst. Without more detailed knowledge of the morphologies of the platinum crystallites in these systems it is not profitable to try to rationalize these differences in activity.

A similar dependence of the activity of catalysts on dispersion has been observed in the oxidation of ethanol and in the decomposition of hydrogen peroxide to dioxygen and water.[24,29] Boudart established that while the activity of platinum in hydrogenation of cyclopropane was independent of crystallite size, smaller crystallites were much more readily poisoned by $O_2$ than were larger ones.[72] The decrease in activity seen in Figure 1 might thus be due to an intrinsic decrease in activity of the platinum surface atoms ($Pt_s$) with a decrease in crystallite size caused by changes in electronic structure or particle surface morphology, to an increase in their susceptibility to poisoning by dioxygen with a decrease in crystallite size, or to a combination of both factors.[73,74]

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(74) If the highly dispersed catalysts are more easily poisoned by $O_2$, they might deactivate upon prolonged storage by reaction with atmospheric oxygen. Extensive deactivation by air seems unlikely, however, since the activities of these catalysts did not change after storage in air for up to 1 year. It is more likely that the deactivation is occurring only under the reaction conditions.

**TABLE I: Reproducibility of Catalyst Properties**

| support | Pt complex[a] | no. of points[b] | %D mean | %D $S_m$[c] mean | $PROD_T$ mean[d] | $PROD_T$ $S_m$[d] mean | method[e] |
|---|---|---|---|---|---|---|---|
| C | $H_2PtCl_6$ | 3 | 7.6 | 1.24 | 51 | 1.11 | wet |
| $Al_2O_3$ | $H_2PtCl_6$ | 5 | 18 | 0.20 | 20 | 0.17 | dry ($H_2$) |
| $Al_2O_3$ | COD | 8 | 52 | 0.08 | 90 | 0.12 | dry (Ar) |
| $Al_2O_3$ | COD | 5 | 3.3 | 0.45 | 168 | 0.30 | calcined |
| $SiO_2$ | COD | 3 | 23 | 0.66 | 290 | 0.32 | dry (Ar) |
| $SiO_2$ | COD | 7 | 9.6 | 0.22 | 335 | 0.06 | dry ($H_2$) |

[a] COD = $(COD)PtMe_2$. [b] Number of values used to determine the mean. [c] $S_m$ = standard error (95% confidence level) corrected for the small sample size. [d] $PROD_T$ (180 min). $S_m$ = standard error (95% confidence level) corrected for the small sample size. [e] See Experimental Section: dry (Ar) = Ar used as heating gas, dry ($H_2$) = $H_2$ used as heating gas.

To see if catalysts with different dispersions showed different activity independent of poisoning, we examined the *initial* catalytic activities of $Pt/Al_2O_3$ catalysts, covering a wide range of dispersions (Figure 2). The catalysts with lower dispersion had significantly higher initial activities than those with higher dispersion.

Because platinum is expensive, it is practically important to know how efficiently it is used. Figure 1 gives catalytic activities based only on the surface platinum atoms. These data do not show the activity of the catalyst per unit of total platinum in the catalyst. Figure 3 shows plots of $PROD_T$ (180 min) vs dispersion. The catalysts prepared from $(COD)PtMe_2$ with silica gel as the support showed the best combination of dispersion and productivity.

*Reproducibility.* We used several experimental protocols to prepare three or more batches of catalysts under identical conditions. For each method, the values were averaged, and the results are shown in Table I ±95% confidence limits (corrected for the small number of samples).[75] Catalyst preparation by reduction of aqueous $H_2PtCl_6$[8,9] gave the least reproducible results. The dispersions for 9% Pt/C prepared by this method ranged from 5.0% to 12% and the $PROD_T$ (180 min) varied from 28 to 73 mol of alcohol/mol of $Pt_T$. The standard errors for these values were 120% and 110% of the mean, respectively. The wide variations in these activities caused us to examine different catalyst preparations. The method requiring high-temperature calcining of $(COD)PtMe_2/Al_2O_3$ also gave a wide range of dispersions, although the values of $PROD_T$ (180 min) only varied by ±30% of the mean. This technique involved heating the sample in air to red heat followed by reduction at 500 °C in $H_2$, and the extreme conditions used were difficult to reproduce exactly. A milder reduction of $(COD)PtMe_2$ on alumina or silica gel gave a reproducible standard error of ±8–66%. The activity of $Pt/SiO_2$ was reproducible to ±22% of the mean, and the activity (expressed as $PROD_T$) was consistent to within ±6%. These errors are large compared to those found in homogeneous systems but still allow the differences in dispersion and activity to be compared. The $Pt/SiO_2$ catalysts prepared by low-temperature reduction of $(COD)PtMe_2$ impregnated on $SiO_2$ with $H_2$ are clearly the most active on the basis of the total platinum content.

*Kinetics.* Samples were withdrawn during the oxidations and analyzed by glpc using dioxane as the internal standard (Figure 4). Initially the reaction showed a linear change of concentration with time (that is, the kinetics were approximately zero order in the concentration of alcohol). The slope of this line was the initial reaction rate ($r_0$, mmol of alcohol reacted/min). For $Pt/SiO_2$ (Figure 4) the reaction rate began to decrease (as the catalyst deactivated) after ca. 30 min. By the time the reaction was stopped, after 180 min, the rate was near zero. The total amount of alcohol that reacted in 180 min was (for $Pt/SiO_2$) 80–85% ($C_{180}/C_0$ = 0.20–0.15 for 2-propanol). During the entire course of the reaction, the disappearance of 2-propanol (P) could be completely accounted for by the appearance of acetone (A) (i.e., $[A]_t = [P]_0 - [P]_t$). No other products were observed, and within the limits of glpc accuracy (ca. ±5%) all of the original amount of alcohol was either converted to acetone or unreacted.

(75) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 484–485.

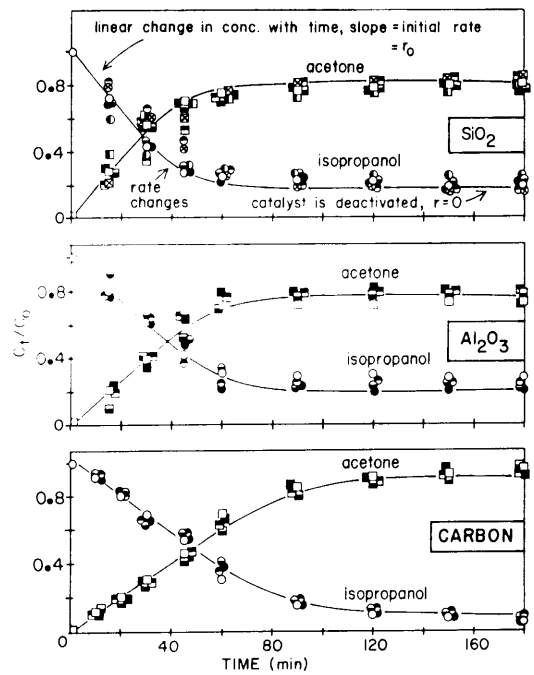


**Figure 4.** Typical oxidations of 2-propanol (P) to acetone (A). Relative concentration vs time: squares = $[A]_t/[P]_0$, circles = $[P]_t/[P]_0$, 1.34 atm of $O_2$, $[P]_0$ = 0.20 M; 1% $Pt/SiO_2$, $D$ = 17%, $Pt_s$ = 2.2 μmol; 1% $Pt/Al_2O_3$, $D$ = 21%, $Pt_s$ = 12 μmol; 9% Pt/C, $D$ = 12%, $Pt_s$ = 17 μmol. For each catalyst, the various points represent replicate runs.

The initial, zero-order, reaction rate ($r_0$) was fairly reproducible. For $Pt/SiO_2$ the results of six duplicate runs were averaged to give $r_0$ = 0.16 ± 0.04 mmol/min (±1 σ) and $C_{180}/C_0$ = 0.19 ± 0.03 (±1 σ). During the reaction the mixture was stirred as rapidly as possible to disperse the catalyst particles. The variations in $r_0$ for $Pt/SiO_2$ were partially caused by differences in the stirring rate (see below). In each case shown in Figure 4 it is clear that the reaction stopped before all of the alcohol had reacted. When carbon and alumina were used as supports, the initial rates were more reproducible. For Pt/C, $r_0$ = 0.10 ± 0.01 mmol/min (±1 σ, average of four runs) while $Pt/Al_2O_3$ gave $r_0$ = 0.13 ± 0.01 mmol/min (±1 σ, average of four runs).

The data in Figure 4 suggest that the rates of reaction are zero order in 2-propanol, but the deactivation of the catalyst during reaction makes it difficult to carry out detailed kinetics over several half-lives. Instead, we examined the kinetics explicitly as a function of the starting concentration of alcohol, using only data taken in the first 2 half-lives of reaction. In this interval, the disappearance of 2-propanol was reliably linear with time (Figure 5), which is expected for a zero-order reaction. The slope yields the rate constant $k = 2.5 \times 10^{-3}$ mol $L^{-1}$ $min^{-1}$. This value of $k$ applies only to this catalyst, but the zero-order kinetic dependence on 2-propanol describes all the catalysts examined.

Figure 6 shows data relevant to the dependence of the initial rate of reaction $r_0$ on the quantity of catalyst present. The behavior of the less active Pt/C catalyst is straightforward. The rate of oxidation of 2-propanol increases linearly with the quantity of catalyst present. The data for the more active $Pt/SiO_2$ system

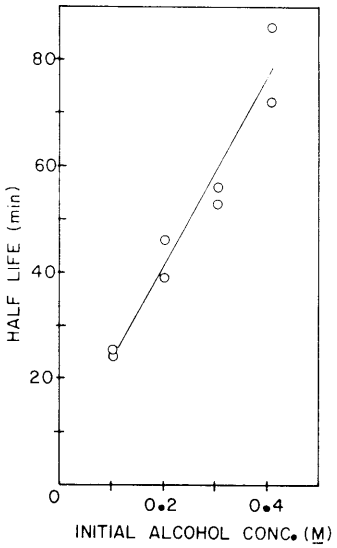


**Figure 5.** Reaction half-life ($\tau_{1/2}$) vs initial concentration of 2-propanol ($[P]_0$): 9% Pt/C, 12% *D*, 17.3 μmol of $Pt_s$, 1.34 atm of $O_2$.

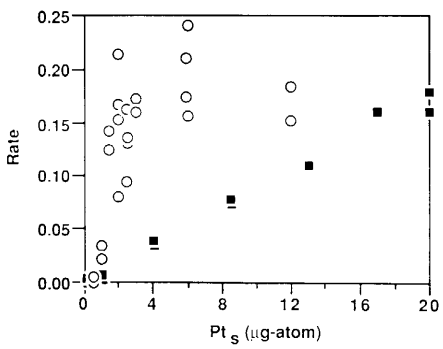


**Figure 6.** Initial reaction rate as a function of the amount of catalyst: 1% $Pt/SiO_2$, 21% *D*, 1.34 atm of $O_2$, $[2\text{-propanol}]_0$ = 0.20 M; 1% Pt/C, 29% *D*, 1.34 atm of $O_2$, $[P]_0$ = 0.20 M.

show significantly greater scatter than do those for the Pt/C system (an observation that we rationalize below as reflecting a high sensitivity of the $Pt/SiO_2$-catalyzed oxidations to the extent of agitation of the reaction mixture, and an insensitivity of the Pt/C-catalyzed oxidation to agitation). Even with the uncertainty introduced by the scatter in the data for the $Pt/SiO_2$ catalyst, it is clear that the form of the plots of $r_0$ vs $Pt_s$ for the $Pt/SiO_2$ and Pt/C catalyst are qualitatively different. More significant kinetically is the observation that the rate of reaction using the $Pt/SiO_2$ catalyst increases (approximately linearly) for small (<5 μmol of $Pt_s$) quantities of catalyst and then abruptly becomes roughly independent of the quantity of catalyst. One rationalization of this observation is that, for high catalyst quantities and fast rates of reaction, the rate of reaction of the $Pt/SiO_2$ catalyst system is limited by the transport of dioxygen to the catalyst surface. We have inferred dioxygen mass transport limitation to rate independently in a kinetically better defined system based on a bulk platinum catalyst.[22]

Figure 7 summarizes the dependence of initial rate of oxidation of 2-propanol on the partial pressure of dioxygen for constant quantities of the Pt/C and $Pt/SiO_2$ catalysts. These two catalysts again showed markedly different behavior. The rate of the faster $Pt/SiO_2$ catalyst varied approximately linearly with $P_{O_2}$; the rate of reaction with the slower Pt/C catalyst was approximately independent of $P_{O_2}$.

The plausible inference from the data in Figure 7 is that these oxidations straddle the line between dioxygen mass-transport limited (MTL) and reaction-rate limited (RRL) processes and are in qualitative accord with the inference from the data in Figure 6. The faster reaction in Figure 7 ($Pt/SiO_2$) is MTL; the slower (Pt/C) is RRL. To test the inference of dioxygen mass transport, we examined the influence of the extent of agitation of the reaction

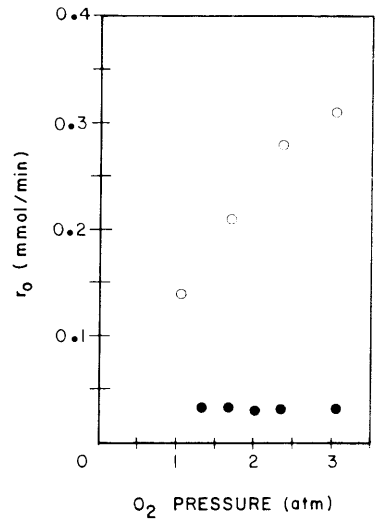


**Figure 7.** Pressure dependence of the initial reaction rate. ○ = 1% $Pt/SiO_2$, 17% *D*, $Pt_s$ = 2.2 μmol, $[P]_0$ = 0.20 M; ● = 9% Pt/C, 7.3% *D*, $Pt_s$ = 8.3 μmol, $[ROH]_0$ = 0.20 M.

mixture on the initial rates. As expected, the rate of the more active $Pt/SiO_2$-catalyzed reaction increases with increasing agitation and rate of dioxygen mass transport to the catalyst; the rate of the less active Pt/C-catalyzed reaction was independent of agitation and was plausibly limited by some step occurring at the catalyst surface, rather than by dioxygen mass transport.

These data provide a simple explanation of the difference in the scatter of the estimates of $r_0$ for the Pt/C and $Pt/SiO_2$ catalysts in Figure 6. All of these reactions were stirred with a magnetic stirring bar, and the extent of agitation was not entirely constant or reproducible. The slower, RRL oxidations catalyzed by Pt/C are insensitive to agitation and thus to variation and irreproducibility in stirring rate. The faster, MTL oxidation catalyzed by $Pt/SiO_2$ are sensitive to agitation, and the scatter in the data of Figure 6 reflects this sensitivity.

The data in this section define two patterns of kinetic behavior. Reactions catalyzed by the Pt/C catalyst used here follow the rate law summarized in eq 7. Those catalyzed by $Pt/SiO_2$ catalysts

$$-d[P]/dt = k_{Pt/C}\omega^0 Pt_s^1[P]^0[P_{O_2}]^0 \quad (7)$$

$$-d[P]/dt = k_{Pt/SiO_2}f(\omega)\ g(Pt_s)[P]^0[P_{O_2}]^1 \quad (8)$$

are described by eq 8. In both equations, $\omega$ refers to the agitation of the system; $\omega^0$ indicates that the rate is independent of stirring; $f(\omega)$ indicates that there is a significant dependence. The expression $g(Pt_s)$ in eq 8 implies only that the rate depends on the exposed platinum surface area.

Equation 7 is that expected for a process whose rate-limiting step involves a reaction of 2-propanol or acetone and the catalyst surface and in which the catalyst surface is fully saturated with adsorbed 2-propanol over the full range of concentrations examined. Other work suggests cleavage of the secondary C–H bond of 2-propanol as rate limiting.[22,23] Equation 8 is compatible with a mechanism in which mass transport of dioxygen to the catalyst surface is overall rate limiting.

*Dependence of Rate on pH.* A study of the dependence of the initial rate of oxidation of 2-propanol for two Pt/C catalysts on pH established that the rate was effectively independent of pH. Use of bromide-, chloride-, or iodide-containing acids or salts strongly suppressed the oxidation, presumably by coordinating with and poisoning the catalyst surface. Fluoride ion has no effect on the rate of oxidation.

*Temperature Dependence of the Rate.* We determined initial zero-order rates for temperatures between 8.9 and 54.0 °C using 5% Pt/C (Figure 8). The reaction rate increased with temperature; the reaction had an activation energy of 9.1 ± 0.2 kcal/mol (±standard error at 95% confidence level determined from the standard deviation of the slope). The preexponential factor was (4.7 ± 0.1) × $10^{10}$ mol/(mol of $Pt_s$ s).

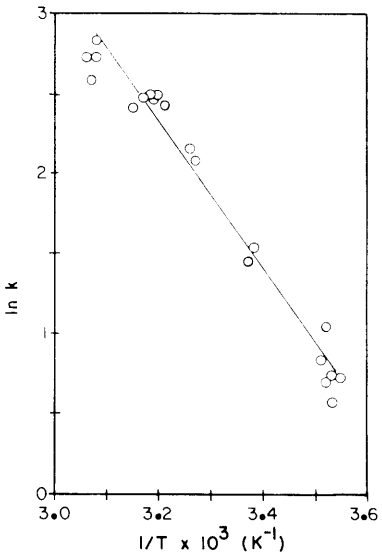


**Figure 8.** Arrhenius plot for the oxidation of 2-propanol to acetone with 5% Pt/C: 10% *D*, 7.8 μmol of $Pt_s$, 1.34 atm of $O_2$, $[2\text{-propanol}]_0$ = 0.20 M; temperature range 54.0–8.9 °C (327–282 K). The rate equation was $-d[P]/dt = k[Pt_s]$: $E_a$ = 9.1 ± 0.2 kcal/mol, $A$ = (4.7 ± 0.1) × $10^{10}$ mol/(mol of $Pt_s$ s); values are ±standard error (95% confidence level) determined from the standard deviation of the slope and *y* intercept.

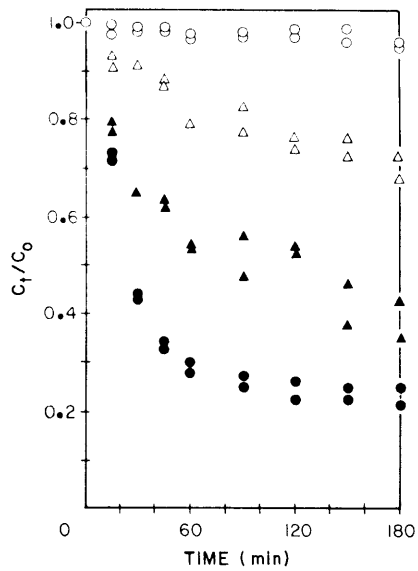


**Figure 9.** Effect of 3 h of $O_2$ pretreatment on aqueous suspensions of catalyst. Relative 2-propanol concentration vs time: 1.34 atm of $O_2$, $[P]_0$ = 0.20 M; 1% Pt/$SiO_2$, 17.7 *D*, 2.2 μmol of $Pt_s$; ○ = $O_2$ pretreatment, ● = no $O_2$ pretreatment; 9% Pt/C, 5% *D*, 15 μmol of $Pt_s$, △ = $O_2$ pretreatment, ▲ = no $O_2$ pretreatment.

Nagai and Gonzalez[76] reported activation energies of 10–13 and 7.4–10 kcal/mol for the oxidation of EtOH and acetaldehyde, respectively, with $O_2$ on Pt/$SiO_2$. Schwartz et al.[26] found that the gas-phase oxidation of 2-propanol to acetone with platinum had an activation energy of 12.8 kcal/mol. Wieckowski[68] reported the $E_a$ for electrooxidation of methanol with platinum in water to be 8.4 kcal/mol. Constantinescu and Brinzoi[60] reported that the adsorption of methanol and ethanol from water onto platinum had $E_a$ = 9 and 7 kcal/mol, respectively. McKee[43] gave an activation energy of 14.3 kcal/mol for the dehydrogenation of methanol on platinum black. These previously reported values are consistent with ours.[77]

*Hydrogen Acceptors Other Than Dioxygen.* Wieland[69] reported that quinone or methylene blue could be used in place of $O_2$ as hydrogen acceptors for platinum-catalyzed oxidation of alcohols, and Alam and Umar[78] have described the oxidation of several alcohols with Raney nickel using benzaldehyde, ethyl acetoacetate, and *trans*-4-phenyl-3-buten-2-one as hydrogen acceptors. We have verified that methylene blue can act as a hydrogen acceptor. After 6 days under argon, a 0.10 M solution of 2-propanol in 0.2 M aqueous methylene blue in the presence of 10% Pt/C produced 3.7 mmol (35%) of acetone. When the amount of catalyst was reduced by 60%, the amount of acetone produced dropped by 60%. Mechanisms that require chemisorbed oxygen for reaction to occur are incompatible with these results.

We evaluated a number of substances—water-soluble *p*-quinones, olefins, dyes, Fremey's salt—as oxidants to replace dioxygen. None was effective. The only active oxidant was hydrogen peroxide, and since platinum catalyzes the rapid decomposition of this compound to dioxygen and water, we cannot distinguish hydrogen peroxide from dioxygen as an oxidant.

*Catalyst Deactivation.* The kinetic data in Figure 4 show that deactivation seemed unimportant in the first 2 half-lives, but all three catalysts became inactive by the time that 80–90% of the 2-propanol had been converted to acetone. Using larger quantities of catalyst did not result in higher conversion.

A number of factors might contribute to the deactivation of the catalyst: oxidation of the surface of the small platinum particles to an inactive or less active platinum oxide; competitive adsorption of acetone or some strongly adsorbing but minor byproduct on the catalyst surface; leeching of strongly adsorbing halide- or sulfur-containing species from the support. We have found no evidence for the last, but the first two may both be important.

Several previous studies[12,14,20,30] have suggested that oxidation of the platinum surface is a factor in the catalyst deactivation. Jaffe and Pleven[20,30] correlated the partial pressure of dioxygen with the number of times a catalyst sample could be reused and reported that the lifetime of the catalyst could be extended by running the reaction under oxygen starvation conditions. Müller and Schwabe also suggested a connection between adsorption of dioxygen on the platinum surface and deactivation of the catalyst.[70]

As a test of the influence of dioxygen on the activity of the catalyst, samples of Pt/$SiO_2$ and Pt/C (not previously treated with $H_2$) were suspended in water under a positive pressure (1.34 atm) of dioxygen for 3 h (the normal reaction time) before addition of 2-propanol. Additional samples of each catalyst were used as controls under standard conditions, in which the 2-propanol was added to the suspension of catalyst *before* the flask was purged with $O_2$ (Figure 9). Both Pt/C and Pt/$SiO_2$ were clearly deactivated by the pretreatment with dioxygen. This deactivation is probably due to formation of an unreactive platinum oxide layer on the surface of the catalyst and has been clarified by electrochemical studies in related systems.[22] Water is important in this deactivation. The catalysts were stored in air and had ample time (up to 1 year) to react with $O_2$ before they were used. Despite this fact and with no activating pretreatment (other than exposure to 2-propanol), they were effective catalysts. In contrast, the same catalysts were deactivated after only 3 h under $O_2$ when suspended in water. Water may allow the metal surface to become hydrated and to form a thicker oxide coating than that formed on the dry catalyst. This view is supported by our electrochemical studies.[22]

Qualitative observation of the appearance of the catalyst under various conditions supports the hypothesis that platinum oxides are important. When the Pt/$SiO_2$ catalyst, after storage in air, was suspended in deoxygenated water without any pretreatment it formed a brown suspension, with color similar to that of $PtO_2$;

(76) Nagai, M.; Gonzalez, R. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 525–531.

(77) This activation energy is much lower than the value reported for the oxidation of methanol on copper. Wachs and Madix[34] reported that this gas-phase reaction had $E_a$ = 22.1 kcal/mol for the formation of formaldehyde. Benziger and Madix[48] reported the oxidation of methanol and ethanol on iron had activation energies of 25.1 and 26.6 kcal/mol, respectively. These authors also reported that isopropyl alcohol did not readily oxidize on these metals. Kvashniva and Yukelson[42] reported the gas-phase dehydrogenation of ethanol and isopropyl alcohol with Raney copper had activation energies of 19.4 and 11.0 kcal/mol, respectively. Mears and Boudart[40] dehydrogenated 2-propanol to acetone with nickel boride in the liquid phase and found the reaction had an activation energy of 20.5 kcal/mol. All of these reactins were performed with catalysts and reaction conditions different from those used in the present study.

(78) Alam, M.; Umar, M. *Pak. J. Sci. Ind. Res.* **1980**, *23*, 140–143.

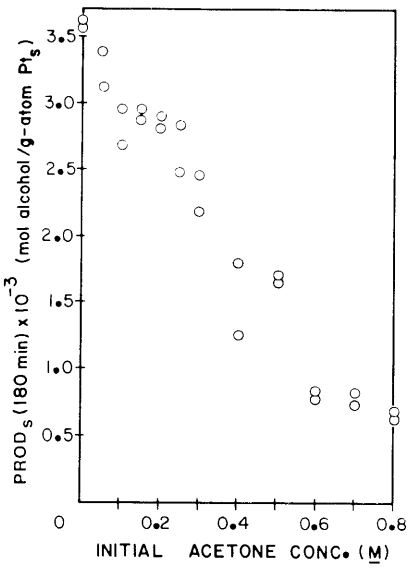


**Figure 10.** Inhibition of the oxidation of 2-propanol by acetone PROD$_s$ (180 min) as a function of initial acetone concentration: 1% $Pt/SiO_2$, 17% *D*, 2.2 μmol of $Pt_s$, 1.34 atm of $O_2$, $[P]_0$ = 0.20 M.

we assumed the color to be due to an oxide coating on the platinum. When 2-propanol was added, the color turned from brown to black within 30 s. If the dry catalyst were treated with $H_2$ in the flask prior to addition of water, the suspension was black, not brown, even before alcohol was added. The catalysts pretreated with $H_2$ showed the same activity as those used without treatment with $H_2$. Thus, addition of 2-propanol was apparently able to reduce at least certain platinum oxides to platinum(0), and treatment of catalyst oxidized dry in air with $H_2$ or with 2-propanol had the same effect.

These qualitative studies thus indicate that deep oxidation of the platinum catalysts with dioxygen in water leads to deactivation that cannot be reversed by reduction with 2-propanol but that the more superficial oxidation resulting from exposure of the catalysts to air at ambient relative humidity is as readily reversed by reduction with 2-propanol as with dihydrogen. These studies, in agreement with other work, identify irreversible (by 2-propanol) oxidation of the platinum as one plausible mechanism of deactivation of the catalyst during operation. Other factors are, however, probably at least as important.

Several reports have indicated that the dehydrogenation of 2-propanol on nickel[39,40] was inhibited by acetone. Dirkx[12-14] reported that the oxidations of D-glucose and D-gluconic acid were inhibited by side products of the reaction. Druz[15] claimed that the oxidation of ethanol to acetic acid with platinum was inhibited by traces of polymers formed from the intermediate acetaldehyde. Wood et al.[44] reported that the gas-phase dehydrogenation of 2-propanol to acetone on platinum was inhibited by carbon monoxide that was formed if traces of oxygen were present in the system. To determine if compounds that acted as catalyst poisons were being formed during the reaction, we tested the effect on fresh catalyst of a reaction solution obtained after 180 min of oxidation of 2-propanol using the standard protocol. The oxidation (1% $Pt/SiO_2$, *D* = 17%) was conducted for 180 min, at which time ca. 25% of the 2-propanol remained. The used catalyst was separated, and fresh catalyst added: no further reaction occurred.

Figure 10 establishes that acetone inhibits the oxidation of 2-propanol catalyzed by $Pt/SiO_2$ but that high concentrations of acetone are required before the inhibition becomes serious. These data, we presume, reflect competitive adsorption of 2-propanol and acetone on the platinum surface. They suggest that acetone is only slightly less strongly adsorbed than 2-propanol: the PROD$_s$ (180) for oxidation of 0.2 M 2-propanol is reduced by a factor of 2 in the presence of 0.3–0.4 M acetone (acetone:2-propanol ≃ 1.5–2.0) and by a factor of 7 for 0.8 M acetone (acetone:2-propanol ≃ 4). The ratio of acetone to 2-propanol at the conclusion of an oxidation under our standard conditions is ca. 6, and

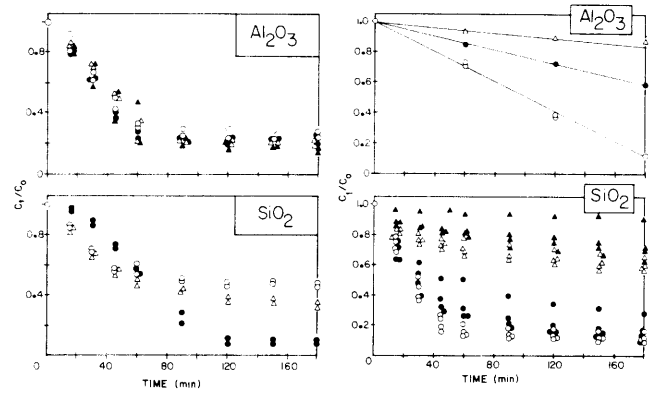


**Figure 11.** Treatment of deactivated catalyst with $H_2$ (1 atm, 1 h) is partially successful in regenerating activity (right); treatment at 1 atm, 230 °C is more successful. The curves are kinetic runs for oxidation of 2-propanol under standard conditions. 1.34 atm of $O_2$, $[P]_0$ = 0.20 M; 1% $Pt/Al_2O_3$, 39% *D*, 89 μmol of $Pt_s$; 1% $Pt/SiO_2$, 21% *D*, 5.6 μmol of $Pt_s$; ○ = first use, ● = second use, △ = third use, ▲ = fourth use.

competitive inhibition could thus, in principle, be severe.

Although our glpc analysis showed no products other than acetone from the oxidation of 2-propanol, other compounds are certainly formed in trace quantities. Such compounds might also be catalyst poisons. Qualitative tests established that oxalic acid (0.01 M) and mesityl oxide (0.01 M) completely inactivated 1% $Pt/SiO_2$ and that acetic acid (0.01 M) and 1,3-dihydroxyacetone (0.01 M) were almost as effective. Brief purging of a reaction mixture with carbon monoxide had no influence on the activity of this catalyst.

*Catalyst Reactivation.* The catalysts deactivate with use, and we were interested in establishing protocols that would permit their reactivation. Simple washing of deactivated catalyst with water regenerated only ca. 10% of the original activity. Treatment of the isolated, washed catalyst with $H_2$ under mild conditions was more effective (Figure 11). Samples of $Pt/SiO_2$ and $Pt/Al_2O_3$ were subjected to repeated use in the oxidation of 2-propanol. After each cycle of use, they were isolated by filtration, washed with distilled water, treated with $H_2$ (1 h, 1 atm), and reused. Although some activity was regenerated on this treatment, the recovered activity progressively decreased. Nonetheless, this procedure is substantially more effective than simple washing in regenerating catalytic activity and confirms that some portion of the loss in activity can be attributed to oxidation of the platinum.

Because mild reductive treatment was only partially successful in restoring catalytic activity, we tried more severe conditions capable both of reducing kinetically stable platinum oxides and of removing strongly adsorbed organic catalyst poisons. The samples of catalyst were reisolated after use, dried, heated in a hydrogen atmosphere to 230 °C, cooled, and reused (Figure 11). These more extreme conditions largely restored the catalyst activity. For $Pt/Al_2O_3$, the regeneration returned the catalyst to its original activity; the dispersion of the platinum did not change in this procedure. When $Pt/SiO_2$ was treated under these conditions, the specific activity, based on $Pt_s$, actually increased above that of the original run, but a change in dispersion accompanied the high-temperature treatment with $H_2$. The original catalyst had a 26% dispersion. After the first cycle of regeneration it decreased to 6.6%; after the second, to 2.1%. Further cycles of reaction and regeneration were not run since the catalyst was not stable under these conditions. We conclude that treatment with $H_2$ at 230 °C is an effective method of regenerating $Pt/Al_2O_3$ but not suitable for $Pt/SiO_2$.

## Discussion

The work in this paper had two objectives. First, we wished to examine the characteristics of oxidations carried out using practically useful catalysts—platinum dispersed on supports—to see if the inferences we could draw concerning the mechanism of the reaction under these conditions agreed with those from mechanistically better defined studies using bulk platinum and

electrocatalytic techniques.[22,23] These complimentary studies indicate that, at a platinized platinum wire catalyst, the reaction should be considered as a catalytic dehydrogenation of alcohol to ketone by reaction with Pt(0), with a separate, coupled step involving oxidative regeneration of Pt(0) by reaction of platinum surface hydride with dioxygen, either directly or by a local cell mechanism. Second, we wished to be able to suggest and/or rationalize protocols for extending the catalyst lifetime in operation and for regenerating its activity once deactivated.

The most useful method for preparing the supported catalysts seemed to be reduction with $H_2$ of (1,5-cyclooctadiene)dimethylplatinum(II) impregnated on the support. This procedure had the advantage that it did not introduce chloride ion (a poison) into the system, as would $K_2PtCl_6$ or related platinum precursors. Of these catalysts, the most useful was $Pt/SiO_2$ having a relatively low dispersion ($D$ = 10%). The $Pt/SiO_2$ catalysts were significantly more active than Pt/C and $Pt/Al_2O_3$ catalysts. We have not carried out the detailed studies of the morphologies of the platinum particles on these supports that would be the necessary first step in rationalizing these differences.

Although all these catalysts deactivated during oxidations of 2-propanol to acetone, it was possible to get adequate kinetic information on all three by using initial rates: in the first 1 or 2 half-lives of reaction, catalyst deactivation was not serious. The reactions were sufficiently rapid to be on the border between mass-transport limited (MTL) in dioxygen, and reaction-rate limited (RRL) by a step taking place on the catalyst surface. Catalysts with high activity ($Pt/SiO_2$) were normally MTL; those with low activity (Pt/C) were normally RRL, but the reactions could be moved from one regime to another by changing conditions. For example, decreasing the quantity of $Pt/SiO_2$ catalyst present in a reaction mixture sufficiently moved the reaction from MTL to RRL (Figure 6). RRL reactions were zero order in both 2-propanol and dioxygen (eq 7). This rate law indicates that the surface of the catalyst is saturated with adsorbed 2-propanol (over the limited concentration range studies: 0.2 ± 0.1 M) and is compatible with the inference from our studies[22,23] and those of others that cleavage of a C–H bond is overall rate limiting.[35,36,76] The observation that acetone is inhibitory at high concentrations indicates that it adsorbs competitively with 2-propanol at the catalyst surface. The reaction is not influenced by the pH of the solution over a wide range of values. The only oxidant other than dioxygen that seems to have any practical value is hydrogen peroxide,[22] but results obtained with this substance are difficult to interpret since platinum is an efficient catalyst for the disproportionation of hydrogen peroxide to dioxygen and water.

The qualitative agreement between the kinetic/mechanistic features of the oxidations of 2-propanol at the supported catalysts and those at a platinized platinum wire catalyst/electrode lead us to infer that these reactions, under different conditions, are sharing a common mechanistic manifold. Labeling and regiochemical studies using Adams catalyst[23] are, we believe, also comparable, although we have not examined the kinetics of these reactions.

The most important practical conclusions from this work concern catalyst lifetime. We conclude that platinum catalysts having relatively low dispersion ($D \simeq 10\%$) represent the best compromise between use of platinum and catalyst lifetime. Catalysts having higher dispersion seem to deactivate rapidly by irreversible oxidation (it might be possible to minimize this oxidative deactivation by using low concentrations of dioxygen[30]); catalysts with lower dispersion are more stable but are required in larger quantity to provide a useful surface area of platinum. Deactivation of the catalyst in operation seems to have at least three components: irreversible oxidation of the platinum surface in small platinum particles; reversible inhibition in situ by competitive weak adsorption of acetone; perhaps irreversible (or slowly reversible) inhibition by strong adsorption of other, minor byproducts of reaction (in our limited studies, carboxylic acids seem to be strongly inhibitory).

Oxidation of small platinum particles by dioxygen seems to be much more extensive for particles in water than in ambient air, and it seems more important for small than large particles. Both inferences are qualitatively reasonable, but a detailed understanding of the thermodynamics and kinetics of oxidation of platinum by dioxygen and hydrogen peroxide as a function of platinum cluster size and shape and of solvation would be very useful in rationalizing the behavior of these catalysts.

It seems practical to regenerate deactivated catalysts by using straightforward protocols, although we have not optimized the regeneration procedures. Simple washing of deactivated catalyst to remove weakly adsorbed inhibitors (e.g., acetone in the oxidation of 2-propanol) is not effective. Treatment of the deactivated, washed catalyst under mild reducing conditions ($H_2$, 1 atm, 27 °C) has a significant effect in regenerating activity. Rigorous reducing conditions (1 atm, 230 °C) regenerates activity completely; some part of the recovery of activity under these conditions is probably due to pyrolysis and volatilization of adsorbed organic inhibitors. High-temperature reduction must be used carefully, however, since the dispersion may change under these conditions.

## Experimental Section

*General.* Chloroplatinic acid,[79] $K_2PtCl_4$,[79] and $(COD)PtMe_2$[80] were prepared according to procedures in the literature. Acetone and 2-propanol were reagent grade and used without further purification. Dioxane was reagent grade and was distilled from $NaBH_4$ before use. Water was doubly distilled and deoxygenated by purging with argon for 20 min before use. Reaction samples were analyzed by using a Perkin-Elmer Model 3920B gas chromatograph equipped with a Precision Sampling Model 4900 automatic sampler.

*Catalyst Supports.* γ-Alumina and large-pore silica gel were purchased from Strem Chemicals, Newburyport, MA. These supports were fine powders with surface areas of 225 and 340 $m^2/g$, respectively, reported by the manufacturer. Darco G-60 activated carbon was purchased from Fisher Scientific Co., Medford, MA. The surface area was not reported. The supports were used as received from the manufacturers. Activated carbon purchased from Strem Chemicals was unsuitable due to its high sulfur content (determined by sodium fusion).

*Typical Catalyst Preparation (Wet Method).* To a solution of 2.61 g (5.04 mmol) of $H_2PtCl_6 \cdot 6H_2O$ in 180 mL of distilled water was added 9.95 g of activated carbon. Hydrogen was bubbled through the stirred mixture at ambient temperature for 1 h. The catalyst was isolated by suction filtration, washed with 500 mL of distilled water, and dried in vacuo to give 10.9 g of 9% Pt/C. The catalyst was not pyrophoric: metal dispersion = 12%; $PROD_s$ (180 min) = 612 mol of alcohol/mol of $Pt_s$. The activity did not change after 1 year of storage in air.

*Typical Catalyst Preparation (Dry Method).* To a solution of 0.854 g (2.56 mmol) of $(COD)PtMe_2$ in 400 mL of pentane was added 49.5 g of silica gel. The solvent was removed under reduced pressure, and the solids were dried in vacuo. A 10-g sample of this impregnated support was placed in a 25-mm o.d. Pyrex tube. The tube was purged with argon and placed in a tube furnace preheated to 240 °C. The material was reduced with a stream of $H_2$ for 3 h and then cooled to room temperature in a stream of argon. During the heating period either $H_2$ or argon was continuously passed through the tube. The catalyst (1% $Pt/SiO_2$) was a gray powder that was not pyrophoric: metal dispersion = 17%; $PROD_s$ (180 min) = 3420 mol of alcohol/mol of $Pt_s$. The catalytic activity did not change after storage for 7 months in air. When $H_2PtCl_6$ or $K_2PtCl_4$ was reduced with this procedure, water was the solvent and reduction was performed at 500 °C.

*Typical Catalyst Preparation (Calcining Method).* The procedure described above (dry method) was used to impregnate 14.9 g of $\gamma$-$Al_2O_3$ with 0.257 g (0.77 mmol) of $(COD)PtMe_2$. A 2.0-g

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sample of this impregnated support was placed in a 10-mL crucible and heated in air with a Fisher burner to dull red heat for 15 min. After cooling, it was reduced with $H_2$ at 500 °C for 3 h in a Pyrex tube placed in a tube furnace. The catalyst (1% $Pt/Al_2O_3$) was a gray powder: metal dispersion = 4.3%; $PROD_s$ (180 min) = 5760 mol of alcohol/mol of $Pt_s$.

*Typical Oxidation of 2-Propanol.* The catalyst sample (0.2–1.0 g) was placed in a 100-mL flask equipped with a Teflon-coated magnetic stirring bar. The flask was capped with a rubber septum and purged with argon. Deoxygenated doubly distilled water (45 mL) and a stock solution (5 mL) that was 2.0 M in both 2-propanol and 1,4-dioxane (an internal glpc standard) were added by syringe. The reaction was started by purging the solution with $O_2$ for 2 min. A positive pressure of 5 psi was then maintained for the duration of the experiment. The mixture was stirred vigorously to keep the catalyst completely suspended in the solution. Samples of the reaction mixture (ca. 0.5 mL) were withdrawn by cannula directly into 1-mL autosampler vials capped with rubber septa. When the samples were taken, both solution and catalyst were withdrawn. The catalyst-to-solution ratio remained constant. The samples were diluted with 1 M NaCl to quench the reaction and fill the vial. The solids were compacted by centrifugation, the vials were sealed, and the solutions were analyzed by glpc: a 9-m × $^1/_8$-in. stainless steel column of 2% Carbowax 20M on 80-100 Chromsorb S, 65 °C.

As a test of the effect of $H_2$ pretreatment, the reactions were run in the same fashion except the flask with dry catalyst was flushed with $H_2$ for 15 min before water and stock solution were added.

*pH-Rate Experiments.* These reactions were done in almost the same way as described above. An aqueous solution of acid or base was made, and its pH was measured with a Radiometer Model PHM62 pH meter. The solution was deoxygenated by purging with argon for 20 min and then used as the solvent. The reactions were run using the standard procedure.

*Inhibition by Halide.* The reaction was run in the standard fashion using 0.1 M potassium halide aqueous solution as the solvent.

*Inhibition by Side Products.* The oxidation was run using the standard method except the aliquots were diluted with doubly distilled water instead of 1 M NaCl. The amount of catalyst was chosen to give ca. 50% reaction. After the aliquots were analyzed by glpc, they were combined with the solution remaining in the flask. The catalyst was compacted by centrifugation, and the supernatant liquid was decanted back into the reaction flask. A fresh catalyst sample was added and the reaction was continued.

As a test of the effect of possible catalyst poisons, the reaction was run using the standard procedure. An aliquot was withdrawn after 10 min of reaction to verify that the catalyst was active. A 0.5 M solution (1.0 mL, 0.5 mmol) of the compound to be tested (such as oxalic acid) was then injected into the flask. The reaction was followed for another 50 min by glpc.

*Catalyst Reuse.* The reaction was run using the standard procedure to see if the catalyst could be reused without any further treatment. The catalyst was then collected by centrifugation and washed with two 20-mL portions of doubly distilled water. The catalyst was returned to the reaction flask, fresh doubly distilled water and stock solution were added, and the reaction was run again using the standard procedure.

*Mild Catalyst Regeneration.* The reaction was run as above for catalyst reuse to see if the catalyst could be regenerated by $H_2$ under mild conditions. The catalyst sample was returned to the flask, fresh water was added, and the system was purged with argon. Hydrogen (1 atm) was bubbled through the suspension for 15–20 min, and the system was again purged with argon. The stock solution was added, and the reaction was run using the standard procedure.

*High-Temperature Catalyst Regeneration.* The procedure of catalyst use and isolation was similar to that described above. After isolation, the sample was dried in an oven at 130 °C. The catalyst was then placed in a 25-mm o.d. Pyrex tube and purged with argon. The gas was changed to $H_2$, and the tube was heated in a tube furnace at 230 °C for 3 h. The catalyst was then cooled in a stream of argon and reused.

*Quinones as $O_2$ Substitutes.* In a typical reaction, 5 mmol of the quinone was placed in a 50-mL flask equipped with a magnetic stirring bar. Doubly distilled water (25 mL) and 0.09 g of 9% Pt/C were added. The flask was capped with a rubber septum and flushed with argon. To this solution was added 5.0 mmol each of 2-propanol and dioxane. The suspension was stirred under a positive pressure of argon for 2 days and analyzed by glpc. No acetone formation was seen with any quinone tested.

*Reaction with Hydrogen Peroxide.* The catalyst (0.27 g, 11% Pt/C) was placed in a 100-mL three-necked flask equipped with a magnetic stirring bar and addition funnel. The system was capped with rubber septa and purged with argon. The flask was charged with 50 mL of doubly distilled water and 10 mmol each of 2-propanol and dioxane. The funnel was charged with 6 mL (50 mmol) of 30% $H_2O_2$. The flask was cooled to 0 °C, and the $H_2O_2$ was added dropwise in 15 min. By the time the addition was complete 9% of the alcohol had been oxidized to acetone. The flask was warmed to room temperature, and the reaction was continued for 5 h to give an 86% yield of product.

*Temperature Dependence of the Reaction Rate.* A 100-mL three-necked flask was equipped with a magnetic stirring bar, reflux condenser, and thermometer. A sample of catalyst (0.300 g, 5% Pt/C, 7.8 μmol $Pt_s$, 10% dispersion) was placed in the flask, and it was capped with rubber septa. The system was purged with argon, and 45 mL of doubly distilled water was added by syringe. The flask was placed in an oil or water bath at the reaction temperature. A stock solution (5.0 mL) containing 9.5 mmol of 2-propanol and 10 mmol of dioxane was added, and the solution was allowed to equilibrate for 0.5 h. The temperature of the solution was noted, and the reaction was run using the standard procedure. At the end of 1 h the reaction was stopped and the solution temperature was noted. An average of the two readings was used. The initial zero-order rate was determined and used to construct the Arrhenius plot.

**Registry No.** Pt, 7440-06-4; 2-propanol, 67-63-0; hydrogen peroxide, 7722-84-1.

*Supplementary Material Available:* Dependence of the initial reaction rate on the stirring rate (Figure S1), reaction rate vs pH (Figure S2), the effect of hydrogen pretreatment on the catalyst activity (Figure S3), and the experimental method for determination of the metal surface area of supported platinum catalysts by titration with dihydrogen and dioxygen (6 pages). Ordering information is given on any current masthead page.