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Platinum Catalyst Deactivation in Low-Temperature Ammonia Oxidation Reactions

I. Oxidation of Ammonia by Molecular Oxygen

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Deactivation of 2.0–15 nm Pt crystallites supported on alumina and Pt black was studied in a fixed-bed differential reactor during NH_3 oxidation by molecular oxygen between 368 and 473°K. Marked deactivation caused by surface oxidation took place during the first 12 hr on stream. Deactivation occurred only in the presence of both reactants. It was more severe with smaller crystallites and at lower temperatures. The rate decay was best described by a second-order deactivation process. At 433°K oxygen present in the deactivated 2.7 nm crystallites was about 5 atoms per surface Pt atom, giving an estimated bulk composition of $PtO_{1.7}$. For the 15.5 nm crystallites the oxygen present in the deactivated crystallites was about 7 atoms per surface Pt atom but the resultant bulk composition was $PtO_{0.5}$. Deactivation was reversible and activity could be restored by raising the temperature above 473°K or by reacting with H_2 or NH_3. Deactivated catalyst slowly released oxygen in reaction with NH_3 chemisorbed on the support after the feed O_2 and NH_3 were turned off. This is a form of reverse spillover. Platinum black studies confirmed the results with the supported catalysts.

INTRODUCTION

The study of hydrocarbon reactions over supported noble metals has been advanced as a result of findings that many, but not all, reactions are structure insensitive; i.e., their specific rate is independent of metal crystallite size (*1*). Contact with oxygen appears to introduce problems even for structure insensitive reactions. Interaction of oxygen with supported Pt before reaction can affect the observed catalytic activity in hydrogenation (*2*) and dehydrogenation reactions (*3*).

For reactions involving oxygen, the situation appears to be more complex. For example, crystallite size significantly affects the specific catalytic activity of supported Pt in the low-temperature oxidation of ammonia (*4,5*).

Boreskov (*6*) reports for studies of hydrogen oxidation over platinum that in an excess of hydrogen the specific catalytic activity at 373°K was the same on Pt wire, Pt foil, and 0.2% Pt on silica with 10 nm crystallites. Reaction over platinum in excess oxygen below 415°K was reported to be particularly complex; the activation energy was dependent on whether the experiments are performed by increasing the temperature (8 kcal/mole) or decreasing it (2.4 kcal/mole). Hanson and Boudart (*7*) observed that in the H_2–O_2 reaction the specific catalytic activity was dependent on Pt crystallite size in excess H_2 but was independent of crystallite size in excess oxygen. McCarthy *et al.* (*8*) report a crys-

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tallite size dependence in CO oxidation over supported Pt in excess oxygen, none in excess CO.

Transient rate behavior is also quite commonly observed. Hall and co-workers (*9,10*) found the kinetics of hydrocarbon oxidation over precious metals showed marked changes with feed gas composition and observed that in the oxidation of ethylene over Pd sponge the rate of reaction responded very sluggishly to changes in gas-phase reactant concentrations. They also reported that the catalyst initially underwent a reversible order-of-magnitude decrease in activity. Tanner and Taylor (*11*) report the development of transient super activity (initiation of $H_2 + O_2$ at 153°K) on heating Pt wire to 1173°K in a vacuum. Other types of transient activity in noble metal oxidation catalysts are the reaction instabilities investigated by Wicke (*12,13*), and the periodic behavior reported by him (*14*) and others (*8,15*) for CO oxidation over Pt. Quantitative understanding of these types of transient behavior is lacking.

Platinum gauzes used in ammonia oxidation initially undergo an activation process (*16*) called thermal faceting by Moore (*17*) and shown by Garton and Turkevich (*18*) to involve extensive surface reconstruction and roughening during reaction. McCabe, Piguet, and Schmidt (*19*) studied the faceting by scanning electron microscopy and propose the term catalytic etching to describe the phenomena since the process is faster and more extensive than is characteristic of etching in the absence of reaction. Presland, Price, and Trimm (*20*) discuss the reorganization of silver films. Grabke (*21*) observed surface reconstruction of iron in H_2O/H_2 mixtures and attributes the effect to the growth of crystal faces whose surface energy has been lowered by oxygen adsorption. Somorjai's recent, carefully controlled studies with single crystals suggest that surface reconstruction is more common with metal catalysts than had been thought (*22*). In the presence of oxygen the situation appears even more complex (*23*). With supported metals loss of metal surface area by sintering (*24*) produces both rapid and long term deactivation.

Break-in phenomena are well known in heterogeneous catalysis and frequently are considered as unavoidable. In many studies of catalyst performance it is standard practice to take data only after a suitable aging period, which may be a number of days. Infrequently is the cause of the initial activity changes carefully explored. With supported metal catalysts the initial activity decline frequently may be associated with loss of active surface area by sintering. However, other causes such as surface reconstruction (*25*) and rapid accumulation of catalyst poisons or carbon may also be responsible (*26*). With metal oxide catalysts, partial oxidation or reduction of the catalyst surface dependent on catalyst pretreatment and on reaction conditions are additional causes.

One of the premises of this work is that it is useful to distinguish between fairly rapid changes occurring on the catalyst surface during the period of development of "steady-state" activity, and those subsequent, relatively slow, alterations of the working surface which are normally considered when discussing catalyst deactivation. These latter changes for metal catalysts may also involve sintering and accumulation of catalyst poisons or carbon. They have a significant economic impact and also considerable literature (*26*).

This work was concerned with characterizing the initial deactivation behavior of supported Pt in the low-temperature oxidation of ammonia.

EXPERIMENTAL METHODS

Apparatus and Procedure

The data were obtained in a differential, fixed-bed flow reactor, which has already been described (*4*). Feed gas consisted of

NH_3 and O_2 in high-purity helium. The exit gas stream from the reactor was analyzed for N_2, N_2O, and O_2 by gas chromatography. Nitrogen levels when pure helium was passed through the reactor system were typically less than 10 ppm, which assured that nitrogen measured was due to reaction.

Rates are reported as turnover numbers which are defined as the number of g-moles of ammonia reacted per g-mole of surface platinum atoms per second. Nitrogen and nitrous oxide formation rates are in terms of g-moles nitrogen or nitrous oxide per g-mole surface sites. The number of surface sites is defined as one-half the total number of surface platinum atoms where the number of surface platinum atoms was determined by hydrogen chemisorption.

Platinum Black Studies

Several runs were performed with platinum black and platinum oxide in a reactor made from a Swagelok tubing union with porous stainless-steel disks in both ends to prevent blowing the extremely fine powder (∼10 nm particles) into other parts of the system. The platinum black was first reduced at 523°K with a 10% hydrogen-in-helium stream to clean the surface. The catalyst was then deactivated under 1% NH_3 and 5% O_2 at 368°K. The catalyst was then rereduced with 10% hydrogen in helium and the deactivation repeated. During the third 10% hydrogen-in-helium treatment, the reactor effluent was passed through a capillary U-tube cold trap at liquid N_2 temperature. The platinum oxide was not reduced prior to contacting with reaction mixture.

Materials

The catalysts were prepared and characterized in our laboratory by Ostermaier (*27*). Characterization included hydrogen chemisorption, oxygen chemisorption, hydrogen–oxygen titration, electron microscopy, and X-ray line broadening. The 1% platinum-on-alumina catalyst, as prepared (unsintered), adsorbed 9.83×10^{-6} g-mole H_2 per gram of catalyst and had a surface average crystallite size of 2.7 nm. A sample of this catalyst sintered at 923°K in air for 24 hr adsorbed 1.71×10^{-6} g-mole H_2 per gram catalyst and had a surface average crystallite size of 15.5 nm.

Helium was high purity, and mixed gases were 6% ammonia and 25% high-purity oxygen, respectively, in high-purity helium. Mixed gases contained <25 ppm nitrogen.

RESULTS

Catalyst Deactivation

As reported previously (*4*), the activity of fresh Pt catalyst declined continuously but at a diminshing rate at temperatures of 433°K or lower. The data are represented by a smooth curve on a plot of the logarithm of the specific catalytic activity vs time [Fig. 1; see also (*4*, Fig. 1)]. A stable, reproducible steady-state activity was reached in less than 12 hr; all steady-state data were taken after 18 hr. Curves for 413 and 433°K were similar, but the extent of deactivation increased with decreasing temperature.

The effect of temperature is best shown by comparing the initial specific rate with

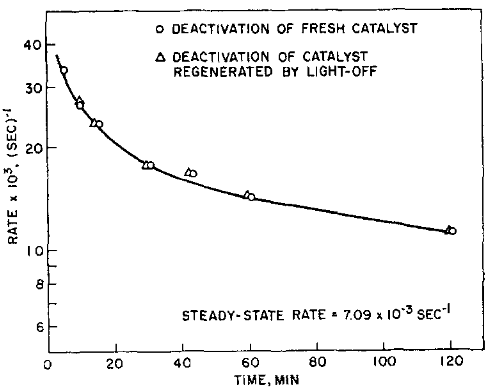


Fig. 1. Deactivation behavior of fresh, unsintered Pt/Al_2O_3 catalyst (○) and of the same catalyst after reactivation by light-off (△): 433°K, 5.0% O_2 and 1.0% NH_3 in He.

TABLE 1

Effect of Crystallite Size and Temperature on Extent of Deactivation

Temp. (°K)	Catalyst	r_I/r_{ss}[a]
393	Unsintered 1% Pt	22
	Sintered 1% Pt	12
413	2.93% Pt, 2.0 nm	12
	Unsintered 1% Pt, 2.7 nm	9.9
	Sintered 1% Pt, 15.5 nm	4.5
433	Unsintered 1% Pt	4.1
	Sintered 1% Pt	1.6

[a] Feed: 1.0% NH_3, 3.0% O_2, r_I = initial rate, r_{ss} = steady-state rate.

the steady-state value. Initial rates were obtained by extrapolating the logarithm of the specific catalytic activity vs time plots to zero time and are believed to be accurate within 20%. Table 1 [from Ref. (*4*)] gives the ratio of the initial to the steady-state rate. Thus, the extent of deactivation increased with decreasing temperature and was typically twice as large for the unsintered 1% Pt catalyst as for the sintered 1% Pt catalyst. The extent of deactivation exhibits Arrhenius behavior with an activation energy of −14 and −18 kcal/mole for the unsintered and sintered Pt catalysts.

Effect of Individual Reactants

The effect of the individual reactants on catalyst activity was investigated by separately passing NH_3 in He and O_2 in He over a fresh catalyst overnight at 433°K. The catalyst was then subjected to the standard reactant feed mixture (1% NH_3, 3% O_2) at 433°K. Neither pretreatment had *any* effect on the initial activity or deactivation behavior, which was the same for both pretreatments as for the fresh catalyst. This does not eliminate the possibility that either O_2 or NH_3 causes catalyst deactivation, but it does show that deactivation is not caused by a simple interaction of either reactant singly with the Pt surface, and that the deactivation is not caused by a trace impurity (poison) in any of the reactant feed gases. The deactivation is associated with the reaction event either through an intermediate formed during reaction or through the energy release occurring during reaction.

Effect of Reactant Concentrations

The effect of relative reactant concentrations on the extent of deactivation was determined by deactivating the Pt/Al_2O_3 catalyst to steady-state activity in an NH_3–O_2 stream containing NH_3 in excess of the stoichiometric requirement, then increasing the O_2 concentration and following the transient behavior. For example, a 1.0% NH_3 and 0.4% O_2 feed gas was passed over fresh, unsintered 1.0% Pt catalyst for 14 hr at 393°K resulting in a steady-state rate of NH_3 oxidation of 0.699×10^{-3} sec^{-1}. The O_2 concentration was then increased to 5.6%, which caused the rate to increase rapidly to 3.40×10^{-3} sec^{-1}. This increase was followed by further deactivation with time. After 12 hr the rate had decreased to 0.589×10^{-3} sec^{-1} and did not change further over the following 12-hr period. When the O_2 concentration was then lowered to 0.5%, the rate dropped to 0.288×10^{-3} sec^{-1} and did not change further with time. This final value of the activity is considerably less than that obtained when a fresh catalyst was deactivated under 0.5% O_2 and 1.0% NH_3. The results are summarized in Fig. 2. Each point is the average of several analyses.

Deactivation thus occurred to a greater extent in a reactant stream containing an excess of oxygen. These results also indicate that the steady-state activity of the catalyst depends on the previous environment to which it was exposed; deactivation in an NH_3-rich environment is less than in an O_2-rich environment. This conclusion was verified in a number of deactivations of fresh catalyst under NH_3-rich and O_2-rich environments.

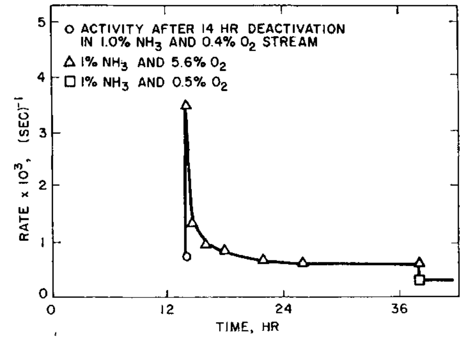


FIG. 2. Effect of feed gas composition on the activity of unsintered Pt/Al_2O_3 catalyst at 393°K; catalyst was first deactivated to steady-state activity (14 hr) with feed gas containing 0.4% O_2 and 1.0% NH_3 in He, feed gas composition was then changed to 5.6% O_2 and 1.0% NH_3 and then back to 0.5% O_2 and 1.0% NH_3.

The extent of deactivation that occurred in an O_2-rich environment did not depend strongly on the absolute value of the O_2 concentration; it only required a significant excess of O_2. For example, fresh unsintered 1% Pt catalyst was deactivated to steady-state activity under a 1.0% NH_3 and 3.0% O_2 stream at 393°K, and the rate was 0.390×10^{-3} sec^{-1}. Another fresh charge of unsintered 1% Pt catalyst was deactivated to a steady-state activity of 0.588×10^{-3} sec^{-1} in a 1.0% NH_3 and 6.0% O_2 stream at 393°K. The O_2 concentration was then reduced to 3.0%, and after 0.5 hr, the activity was 0.421×10^{-3} sec^{-1}, at which time the activity had reached a steady value. These activities are within 10% of each other, indicating that the extent of deactivation is not dependent on the absolute level of O_2 concentration when an excess of O_2 is present in the reactor feed. Also, the reaction rate in a 5.6% O_2 and 1.0% NH_3 stream at 393°K following the sequence of steps given in Fig. 2 was 0.589×10^{-3} sec^{-1} when the steady-state condition was reached. This activity agrees with 0.589×10^{-3} sec^{-1}, obtained by simply deactivating a fresh catalyst in a 6% O_2–1% NH_3 stream at 120°. The data are summarized in Table 2.

These results demonstrate that the condition of the catalyst surface and its activity depend on the reaction environment, and that changing the environment modifies the catalyst surface, sometimes in an apparently irreversible manner. For this reason all deactivations were carried out in an O_2-rich environment for 18 hr, which gave the most stable, most deactivated surface.

Light Off

When NH_3 was oxidized over the catalysts used in this study at 433°K or below, the reaction rate was low enough that intrinsic chemical kinetics are observed. However, for a reactor temperature of 453°K or above, a fresh catalyst, and typical feed composition, e.g., 1.0% NH_3 and 5.0% O_2, the reaction would light-off, giving complete conversion of NH_3, and the reaction rate became mass transfer limited. With light-off the surface composition and temperature change significantly and so did the observed deactivation. Limited data under light-off conditions indicated that deactivation occurred, but very slowly.

TABLE 2

Effect of Deactivation Conditions on Steady-State Activity at 293°K

Deactivation condition	Conditions under which rate was determined	Rate (sec^{-1})
1.0% NH_3 3.0% O_2	1.0% NH_3 3.0% O_2	0.390×10^{-3}
1.0% NH_3 6.0% O_2	1.0% NH_3 6.0% O_2	0.589×10^{-3}
1.0% NH_3 6.0% O_2	1.0% NH_3 3.0% O_2	0.421×10^{-3}
1.0% NH_3 0.4% O_2	1.0% NH_3 0.4% O_2	0.699×10^{-3}
1.0% NH_3 0.4% O_2	1.0% NH_3 5.6% O_2	3.4×10^{-3}

If the unsintered catalyst was deactivated at 433°K, using a 5.0% O_2 and 1.0% NH_3 feed at 500 cm^3/min, the temperature could be raised to 453°K without light-off. However, if the reaction was started using a fresh catalyst at 453°K and the same reaction conditions, light-off occurred and reaction continued at a steady-state NH_3 conversion of 100%. (The adiabatic temperature rise for 100% conversion of a 1.0% NH_3 stream is 130°K.)

Light-off could not be eliminated, nor could the temperature at which light-off occurred be changed by increasing the flow rate from 500 to 1500 cm^3/min, decreasing the catalyst charge from 1.5 to 0.4 g, or by adding 1.5 g of inert Al_2O_3 to 0.4 g of active catalyst. Similarly, a reactor with catalyst operating under light-off conditions could be cooled to temperatures below 433°K before conversion dropped to a low level. This type of instability and hysteresis behavior is consistent with particle multiple steady-state behavior (*28–30*), and such unsteady-state behavior is assumed to be the cause here.

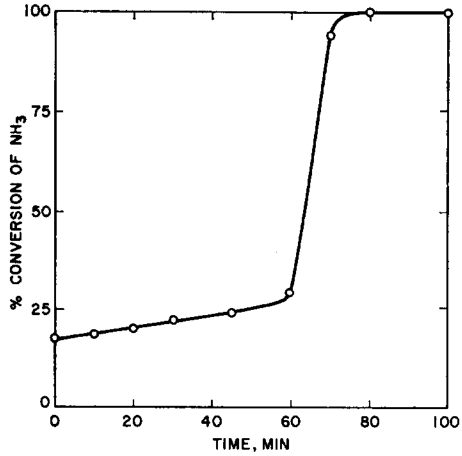


FIG. 3. Behavior of Pt catalyst which had previously been deactivated at 433°K after temperature was increased to 473°K: sintered 1% Pt catalyst, deactivated in 1.0% NH_3 and 3.0% O_2, then feed conditions were changed to 1.0% NH_3, 1.0% O_2 and 473°K.

Restoration of Activity

Effect of increasing temperature. To determine whether deactivation was reversible, unsintered catalyst was deactivated for 24 hr at 433°K, after which the feed temperature was raised to 493°K while the flow of reactants was maintained. This caused the reaction to light-off and this condition was held for 30 min. The NH_3 and O_2 feed gas streams were then turned off, and the catalyst was cooled to 433°K in flowing helium. When the 5.0% O_2 and 1.0% NH_3 feed gas stream was then passed over the catalyst at 433°K, the initial activity and deactivation pattern were identical to that of the fresh catalyst (Fig. 1).

In another experiment, sintered catalyst was deactivated at 433°K for 18 hr in a 3% O_2 and 1% NH_3 stream flowing at 500 cm^2/min. The O_2 concentration was then reduced to 1%, and the bath temperature raised to 473°K which required less than 10 min. The composition of the reactor outlet was followed with time for 2 hr. The conversion of NH_3, shown in Fig. 3, gradually increased and the reaction lit off after 60 min. The increase in conversion with time is caused by increased catalyst activity, which results from removal of the poison formed at 160°C (reactivation of the surface deactivated 160°C). This result, together with the evidence presented previously, suggests that the extent of catalyst poisoning decreases with increasing temperature. This same phenomenon was also observed using the unsintered 1% catalyst.

Effect of gas compoistion.

Helium. An unsintered 1% Pt catalyst (1.46 g) deactivated for 24 hr at 433°K in a 5.0% O_2 and 1.0% NH_3 stream flowing at 500 cm^3/min and had a steady-state rate of 0.760×10^{-3} sec^{-1}. The O_2 and NH_3 were then turned off, and pure He was passed over the deactivated catalyst for 1 hr at 433°K and 500 cm^3/min. Figure 4 shows the N_2 concentration in the reactor effluent as a function of time; no N_2O was detected after 10 min. After He was passed over the catalyst for 1 hr, a 5.0% O_2 and 1.0% NH_3 feed was again passed over the catalyst, and the rate of NH_3 oxidation was followed with time for 2 hr (Fig. 5). Sweeping with He at 433°K for 1 hr caused almost complete reactivation (compare Fig. 5 with Fig. 1). After deactivation for 2 hr, the catalyst had almost returned to the steady-state activity measured after a 24 hr deactivation.

When the sintered 1% Pt catalyst was deactivated to a steady-state activity at 433°K in a 1.0% NH_3 and 3.0% O_2 stream, and then sweep by He at 500 cm^3/min for 1 hr, the results were similar except less N_2 was formed.

Ammonia–helium. After the 2 hr deactivation of the unsintered catalyst of Fig. 5, the O_2 in the feed gas was stopped; and a 1.0% NH_3 stream was passed over the catalyst at 433°K and 500 cc/min for 1 hr. Again the N_2O concentration in the reactor exit stream went to zero in less than 10 min. The N_2 concentration as a function of time followed about the same curve as when the catalyst was swept with pure He, as shown in Fig. 5.

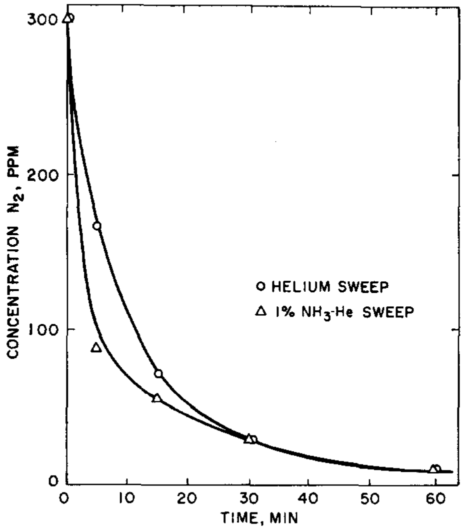


FIG. 4. N_2 concentration in reactor effluent while sweeping deactivated catalyst with He and He–NH_3 stream: unsintered 1% Pt catalyst, deactivation conditions; 1.0% NH_3, 5.0% O_2, 433°K.

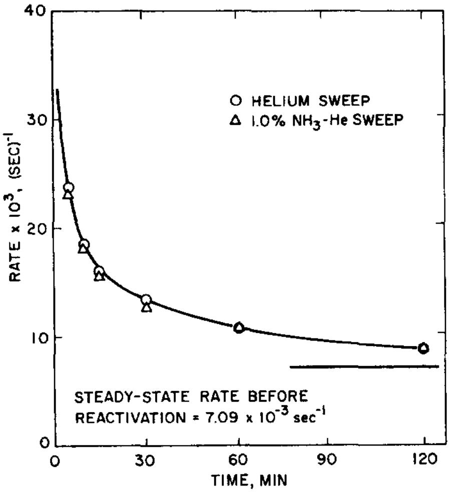


FIG. 5. Catalyst deactivation behavior after 1 hr He sweep and 1 hr He–1.0% NH_3 sweep: unsintered 1% Pt catalyst, reaction conditions; 1.0% NH_3, 5.0% O_2, 433°K.

After the catalyst had been swept with 1% NH_3 in He for 1 hr at 433°K, the catalyst activity and deactivation behavior, when contacted with a 5% O_2 and 1% NH_3 feed gas, were the same as those for the catalyst after the He sweep (Fig. 5) and almost equivalent to the fresh catalyst behavior (Fig. 1). Sweeping with either He or 1.0% NH_3 in He at 433°K caused almost complete regeneration of the deactivated catalyst activity to that of fresh catalyst, and the regenerated catalyst gave the same deactivation behavior when the reaction was again initiated with the standard feed.

Oxygen–helium. When the NH_3 flow was turned off after a standard deactivation and a 1.0% O_2 in He stream was passed over the catalyst, considerable quantities of both N_2 and N_2O were observed in the product stream for at least ½ hr. No N_2O could be detected 10 min after the O_2 flow was discontinued when He or 1.0% NH_3 in He was passed over the catalyst. After the 5.0% O_2 stream was passed over the catalyst for 1 hr, a 5.0% O_2 and 1.0% NH_3 reactant feed was again passed over the

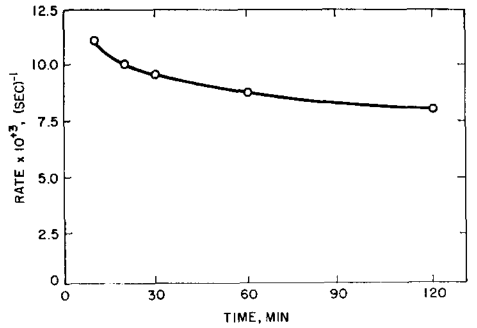


FIG. 6. Catalyst deactivation behavior after 1-hr He–5.0% O_2 sweep: unsintered 1% Pt catalyst, reaction conditions; 1.0% NH_3, 5.0% O_2, 433°K.

catalyst; and the rate was followed with time (Fig. 6). After the deactivated catalyst had been swept with O_2 in He, there was about a 50% increase in activity, compared with a 400% increase caused by sweeping with 1.0% NH_3 in He or pure He. This latter activity increase represents essentially complete reactivation to fresh catalyst activity; that with the O_2 sweep does not.

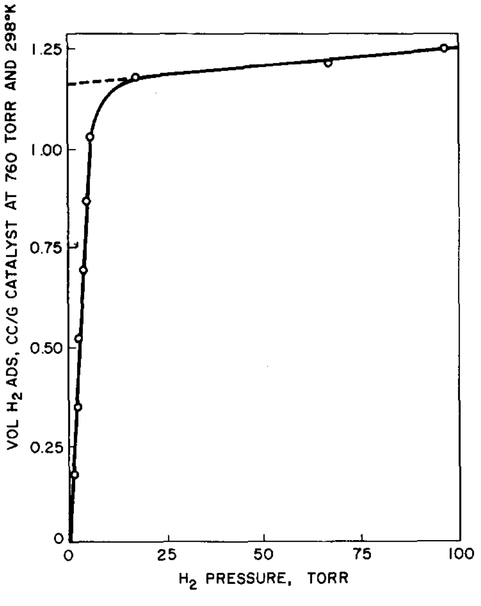


FIG. 7. H_2 adsorption pseudoisotherm for unsintered 1% Pt catalyst which had been deactivated at 413°K; H_2 adsorption was at 298°K, each datum point taken after 12 hr.

To further check the effect of O_2 and handling on restoring catalytic activity, the unsintered catalyst was deactivated for 20 hr at 413°K in a 5.0% O_2 and 1.0% NH_3 stream. The NH_3 was then turned off and a 5.0% O_2 in He stream was passed over the catalyst for 36 hr, after which time no N_2 or N_2O was observed in the reactor effluent. Helium was then passed over the catalyst for 1 hr, and the catalyst removed from the reactor. A portion of this catalyst was then placed back in the reactor, and the transient behavior observed at 433°K. The behavior was similar to that shown in Fig. 6 and showed only about a 25% decrease in activity after 1 hr. Thus, treating a deactivated, unsintered catalyst with O_2 for extended periods and handling it in the air did not regenerate activity or further deactivate the catalyst.

Chemisorption on Deactivated and Fresh Catalyst

To gain further information concerning the state of the deactivated catalyst, the unsintered 1% Pt catalyst, deactivated under standard conditions at 413°K, was examined by H_2 chemisorption. The catalyst was exposed to pure O_2 at 760 Torr and 298°K for 1 hr in the chemisorption apparatus and was then evacuated for 1 hr at 10^{-2} Torr and 298°K. The catalyst was then exposed to repeated doses of H_2 at 298°K, and an adsorption isotherm was determined (Fig. 7). The uptake of hydrogen after each dose was very slow, and 12 hr was allowed between doses. After 12 hr, H_2 adsorption appeared to be continuing, but it was immeasurably slow.

After the pseudoisotherm was completed, the catalyst was evacuated to 10^{-2} Torr and heated to 473°K for 2 hr. Oxygen was then passed over the catalyst for 2 hr at 298°K and 760 Torr, and the catalyst was evacuated to 10^{-2} Torr for 12 hr. A H_2 titration was then performed on the catalyst at 298°K; the results are shown in Fig. 8. The uptake of hydrogen was rapid, as in the titration of a platinum catalyst which had undergone H_2 reduction at 623°K and degassing at 773°K, and had been contacted with O_2 at 298°K. This suggests that the above H_2 treatment partially regenerated the surface.

If Fig. 7 is extrapolated to zero pressure using the three highest pressure points of the titration, the volume of H_2 at $P = 0$ is 1.16 cm^3/g catalyst. Performing the same extrapolation in Fig. 8 for the deactivated catalyst after pumping off and contacting with O_2 and 298 gives 0.47 cm^3 H_2 adsorbed/g catalyst. The zero extrapolation of a hydrogen–oxygen titration performed on a deactivated catalyst after complete (high-temperature) H_2 reduction or on the fresh catalyst gives 0.625 cm^3 H_2/g catalyst (Fig. 8). The amount of H_2 adsorbed by the deactivated catalyst is 1.85 times that adsorbed by a freshly reduced catalyst which had chemisorbed a monolayer of oxygen at 298°K and 2.47 times the H_2 adsorbed by the deactivated catalyst, after H_2 treatment at 298°K, heating to 493°K at 10^{-2} Torr, and exposure to O_2 at 298°K.

The somewhat reduced uptake by the deactivated catalyst after the first H_2 treatment, as compared to the fresh surface, suggests that the above treatment only rereduced about 75% of the surface. Failure to reduce the surface to its original state by treatment with H_2 at 298°K suggests the presence of strongly bound species which are reduced only under more vigorous conditions or bulk platinum compounds. Hydrogen chemisorption on fresh catalyst surface covered with oxygen and on the deactivated catalyst surface after hydrogen treatment at 298°K, evacuation at 473°K, and contact with oxygen at 298°K was very rapid. The slow adsorption of H_2 on the freshly deactivated catalyst at 298°K indicates the presence of a surface species different from chemisorbed oxygen. The H_2 adsorption on the deactivated catalyst represents a hydrogen uptake of 5.6 hydrogen atoms per surface platinum atom if the surface area is the same as that of fresh catalyst as established after high-temperature hydrogen treatment.

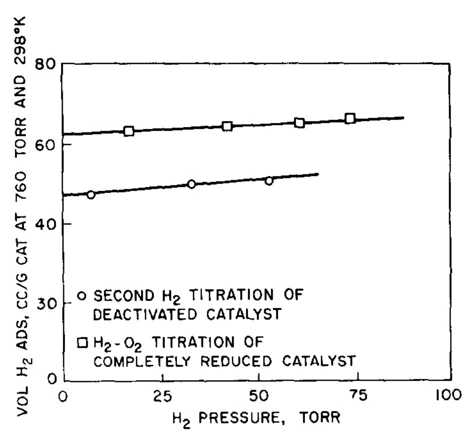


FIG. 8. H_2 adsorption isotherm (H_2–O_2 titration) for deactivated, unsintered Pt catalyst after determination of initial H_2 adsorption isotherm shown in Fig. 7, and H_2–O_2 titration isotherm of unsintered catalyst after complete reduction of catalyst in H_2 at 623°K: isotherms determined at 298°K.

In addition to the reversible deactivation discussed above, there exists the possibility of permanent change in the catalyst caused by sintering, faceting, or crystal migration due to the gas environment or high local temperatures. The surface area of the unsintered 1% Pt catalyst determined by H_2 chemisorption after the deactivated catalyst was reduced in flowing H_2 at 673°K was the same as that observed for the fresh catalyst. This was demonstrated several times. The surface area of the sintered catalyst as measured by H_2 chemisorption was slightly higher after reaction, but the amount of O_2 which chemisorbed was about the same both before and after reaction. The difference in H_2 chemisorption was only slightly greater than the reproducibility of this low surface area catalyst.

The chemisorption measurements show that the platinum surface is completely reactivated by treatment with H_2 at 673°K, since the amounts of H_2 adsorbed before and after reaction are the same. The ability of the catalyst to chemisorb O_2 and catalyze the H_2–O_2 titration reaction at room temperature also supports the fact that high-temperature H_2 reduction is capable of regenerating the surface deactivated during reaction. The constancy of surface area as measured by H_2 chemisorption for the unsintered catalyst indicates that no sintering occurred. The activity of both the unsintered and sintered 1% Pt catalysts was redetermined after use in the kinetic studies and regeneration in H_2 at 673°K. The initial activity of unsintered and sintered 1% Pt catalysts at 393°K was the same for both the fresh and regenerated samples, and the activity after 20 hr was the same, indicating no permanent change in the catalyst had taken place.

Platinum black–platinum oxide studies. A run using Pt black confirmed relatively the same behavior observed for the supported Pt. The Pt black was deactivated under 1.0% NH_3–5.0% O_2 at 368°K several times with regeneration under 10% H_2 in He at the same temperature. Initial activity was not recovered after the first cycle, due probably to sintering of the Pt black; further cycles showed substantial deactivation with most of the activity loss being recovered in the subsequent regeneration under flowing H_2. During one of the regenerations the off-gas was passed through a capillary tube cold trap, and a significant quantity of water was collected. There was no sign that NH_3 was present. The amount of water was not determined quantitatively but was consistent with the amount expected based on a multilayer platinum oxide. Passing the H_2 through the bypass and then through the cold trap demonstrated that the water was not from the H_2–He feed gas. Analysis of the feed also demonstrated that O_2 in the H_2–He feed gas could not have produced the water found. Thus, water resulted from reaction of H_2 with oxygen species on the surface of the deactivated Pt.

The same amount of platinum oxide (PtO_2) gave no measurable conversion ($<0.1\%$) of the NH_3 at 373 and 403°K for 1.0% NH_3 and 5.0% O_2. At 413°K NH_3, conversion became measurable although small, and catalyst activity was observed to increase with time rather than decreasing. Powder surface areas were not measured but are not expected to be greatly different since the materials as obtained consisted predominantly of 10.0 nm crystallites. The platinum oxide was much less active than the Pt black, and the activity which developed appeared to be associated with activation of the surface under reaction conditions. With Pt black or supported Pt these conditions typically gave deactivation.

DISCUSSION OF RESULTS

Cause of Deactivation

Activity decline was due to deactivation of the surface by the reactants during reaction and not to crystallite size growth or poisoning by some other material. The ability to obtain the same surface area by hydrogen chemisorption before and after deactivation (after cleaning the surface with hydrogen) demonstrates that the deactivation was not due to crystallite size growth. That the initial and the steady-state activity were reproduced after reaction-temperature regenerations which were much shorter than the deactivation times suggests that the deactivation is not due to large-scale crystallite rearrangement. The ability to regain the same initial and steady-state activity after the catalyst had lit-off several times also suggests catalyst stability.

Since neither O_2 nor NH_3 alone was capable of affecting the specific catalytic activity, deactivation is not associated with adsorption and interaction of these species with the surface. Deactivation arises from the reaction event between adsorbed ammonia and adsorbed oxygen.

The H_2 titration and purge experiments indicate that the deactivated catalyst contained oxygen because of the observed water formation with hydrogen regeneration of the Pt black and N_2 formation with an ammonia purge of the deactivated catalyst (Fig. 4). We speculate at this point that the deactivation is due to the formation of an oxide on the surface of the platinum and will develop this further below.

One possible explanation for the formation of platinum oxide (deactivation) during reaction, and the absence of deactivation by O_2 alone, is that high local temperatures are generated on the catalyst surface during the reaction event. This elevated local temperature could be responsible for the formation of the oxide. The formation of the oxide could also result from the reaction of active O species formed on the surface during the NH_3 oxidation event with the Pt forming an oxide. These O species formed during reaction could be in a much more active state electronically than chemisorbed oxygen. Fryburg (*31*) has shown that oxygen atoms react with platinum at a much greater rate than oxygen molecules. The absence of significant deactivation at temperatures above 453°K is probably due to the increased ability of NH_3 to maintain the metal surface in a reduced state.

Deactivation in the presence of several species when the single species was inactive for deactivation has been observed by Mills, Weller, and Cornelius (*32*). They found that treating a Pt catalyst with water vapor at 753°K caused no reduction in cyclohexene dehydrogenation activity, but treating it with H_2 and water vapor simultaneously caused a severe reduction in activity. They also found that treating a Pt catalyst with O_2 at 753°K caused only a 15% reduction in cyclohexane dehydrogenation activity but treating it with an SO_2–O_2 mixture at the same temperature caused a complete loss of activity. Part of this activity loss was a result of crystallite growth, but there was an additional loss of activity caused by the SO_2–O_2 reaction taking place on the catalyst.

Our observation of a small amount of deactivation for temperatures above 453°K over the time scale of our experiments (~24 hr) and marked deactivation for lower temperatures is consistent with the literature. Bentsen (*33*) reported exponential decay in NH_3 oxidation over Pt for 60–180 hr periods at 449°K. He did not observe deactivation at 477°K; neither did DeLaney and Manogue (*34*) in integral reactor studies with a 4.3 nm crystallite Pt/Al_2O_3 catalyst over a 27 hr period at 553°K or with a 40 nm crystallite catalyst over a 128 hr period at 573°K.

Correlation of Deactivation Data

In view of the known complexity of metal oxidation reactions, caution is required in interpreting the deactivation kinetics. However, some useful insights can be gained from modeling the deactivation kinetics. First, the rate decay behavior is not well represented by an exponential decay function,

$$r = M_1 e^{-t/M_2}. \qquad (1)$$

An exponential decay function can be shown to result from a first-order site deactivation mechanism,

$$dN/dt = -k_D N. \qquad (2)$$

Even when the rate and M_1 are expressed in terms of the rate increment above the steady-state rate, exponential decay does not represent the rate decay well.

However, since we have already shown that deactivation occurs only during reaction and that the reaction rate is well represented by a two-site Langmuir–Hinshelwood rate expression (*4*), it is logical that the rate decay should also depend on the concentration of site pairs, since the reaction apparently does. For a rate decay dependent on site pairs on the undeactivated metal surface,

$$dN/dt = -k_D N^2, \qquad (3)$$

$$N = N_0/(1 + N_0 k_D t). \qquad (4)$$

Expressing the rate of reaction in terms of the observed rate r minus the steady-state rate r_{ss}, which is considered to be the rate contribution of the undeactivated metal surface, we have

$$(r - r_{ss}) = \frac{N_0}{1 + N_0 k_D t} \cdot k_s, \tag{5}$$

where k_s contains all kinetic parameters including concentration and temperature dependencies. Upon rearrangement, Eq. (5) gives

$$\frac{1}{r - r_{ss}} = \frac{1}{k_s N_0} + \frac{k_D}{k_s} t. \tag{6}$$

Figure 9 shows that the deactivation data for the unsintered Pt catalyst at all three temperatures are well represented by Eq. (6), which clearly suggests that the deactivation process is directly related to the reaction process. However, $k_D N_0$, obtained from Fig. 9, is independent of temperature, suggesting that the rate of deactivation is not directly proportional to reaction rate. This indicates that the deactivation process is a balance of surface processes. Above we showed that NH_3 regenerates the deactivated Pt surface and that higher temperatures result in a lower extent of deactivation including complete activity regeneration upon light-off. Thus, NH_3 appears to be a more effective reducing agent at higher temperatures and any tendency for the deactivation process to increase with temperature could well be offset by an increasing reduction (regeneration) ability of the NH_3.

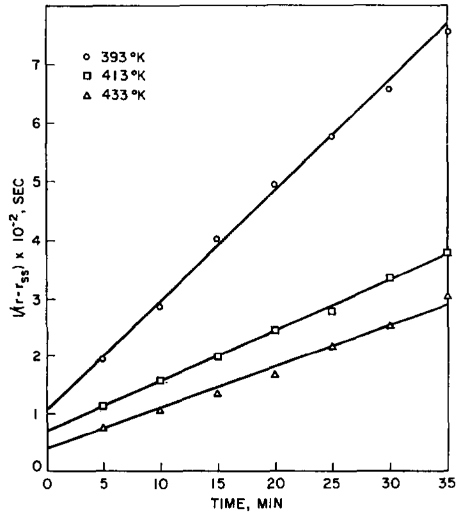


Fig. 9. Correlation of deactivation data accordign to a deactivation process requiring pairs of sites: unsintered 1% Pt catalyst, 1.0% NH_3 and 3.0% O_2.

The achievement of a nonzero steady-state activity after almost 18 hr, and the absence of further deactivation after this time, requires that there be a certain number of sites that are not deactivated, that the rate of formation and the rate of removal of deactivated surface become equal at this point, or that the active surface be no longer platinum metal, but a platinum compound, which is acting as the catalyst. We propose that the deactivation is due to the formation of a Pt oxide, on the surface. The very low activity of PtO_2 in NH_3 oxidation and the slowly increasing activity at 413°K under a standard 1.0% NH_3–5.0 O_2 feed gas (partial surface reduction) suggest that the activity of the deactivated catalyst is due to a partially oxidized (not PtO_2) Pt surface.

Purge Experiments

The purge experiments with He–NH_3 show that the catalyst could be almost completely reactivated by contact with NH_3 forming almost exclusively N_2, just as it could be reactivated by reduction with H_2. We propose that the reactivation is due to an NH_3 reduction of the oxidized Pt surface.

The evolution of measurable amounts of N_2 from the deactivated catalyst for a period of >1 hr after the flow of reactants was stopped, as shown in Fig. 4, suggests the possibility that the deactivation involves both the surface and the bulk of the metal crystallites. This slow evolution of N_2 is similar to the slow uptake of H_2 in the chemisorption experiments. Both could be explained on the basis that the rate-determining step is the rate of diffusion of oxygen to the surface of the platinum crystallite and/or is the extraction of the oxide ion from the surface.

The absence of N_2O suggests that nitrogen could not remove oxygen from the deactivated Pt surface; oxygen removal was accoumplished by the hydrogen from the ammonia. This is consistent with the difficulty of removing oxygen from the deactivated Pt as observed in the H_2 chemisorption experiment in comparison with the ease of removal of chemisorbed oxygen. Tightly bound oxygen on catalytic surfaces typically does not produce much N_2O in NH_3 oxidation [see discussion in Ref. (4)].

The purge experiments with He alone and with He–O_2 indicate that either NH_3 or some adsorbed NH_3-intermediate was present on the alumina surface and was able to diffuse to the metal surface and react, or desorb and then react on the metal surface. This process led to regeneration of the initial activity when a constant source of gas-phase O_2 was not present. The slight reactivation which occurred when the deactivated catalyst was treated with gas-phase O_2 is most likely due to the reaction of species already present on the metal or the support with the deactivated surface during a He purge after the oxygen treatment and not to the action of O_2. If deactivation had been due to a nitrogen-containing species on the Pt, the He–O_2 purge should have resulted in reactivation.

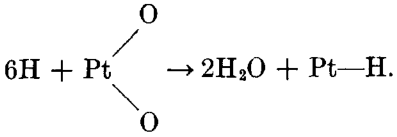
Since there is most likely a considerable amount of NH_3 adsorbed on the alumina (*35*), sweeping with He may be equivalent to sweeping with NH_3 in He; and the regeneration reaction is between NH_3 and the deactivated Pt surface. Bond (*36*) suggests similar back migration of spilled-over hydrogen in discussing experiments in which 1-pentene in N_2 is used to estimate the amount of H_2 on a Pt/SiO_2 catalyst.

The amount of N_2 evolved over a period of 1 hr when the unsintered, deactivated Pt catalyst was swept with He at 500 cm^3/min and 433°K can be obtained by integrating beneath the curve in Fig. 4. This integration yields 5.2×10^{-5} g-moles of N_2/g of catalyst in 1 hr, of which an appreciable amount appears during the first 5 min. Pusateri (*37*) showed that the purge time for the system in similar experiments is less than 2 min, and this work clearly supported his finding. Although a fraction of the N_2 formed during the first 5 min probably comes from the reaction of reactants and reaction intermediates present on the Pt surface, the N_2 formed after this time is almost certainly due to the interaction of NH_3 with the deactivated Pt surface.

The concentration of surface Pt atoms for the unsintered Pt catalyst was 2.0×10^{-5} g-atoms of surface Pt/g of catalyst. A comparison of the amount of N_2 evolved in 1 hr with the number of surface Pt atoms suggests that the oxidative deactivation was not limited to the surface, but extended into the bulk metal of the crystallite. If it is assumed that the Pt surface is initially covered with an adsorbed monolayer of nitrogen-containing molecules and that each two nitrogen-containing molecules yields one N_2 molecule, the amount of N_2 evolved beyond this amount is 4.2×10^{-5} g-moles N_2/g of catalyst. If all of this N_2 is formed by the reaction of NH_3 with oxygen in or on the platinum, then 6.3×10^{-5} g-moles of O_2 (12.6×10^{-5} g-moles O) per g of catalyst are required for the stoichiometry $2NH_3 + \frac{3}{2}O_2 \rightarrow N_2 + 3H_2O$. This is equivalent to about 6.2 atoms of oxygen for each surface Pt atom. If all N_2 formed the first 5 min is neglected, 4.5 oxygen atoms per surface Pt atom are indicated. This clearly indicates bulk oxidation of the small metal crystallites. Similarly, the H_2 chemisorption on the deactivated Pt catalyst indicated more than a surface layer of oxygen, but because it was done at 298°K it did not result in extensive reduction of the metal oxide.

The calculated 4.5 oxygen atoms per surface Pt atom on the 2.7 nm (dispersion = 0.38) Pt crystallites represent 1.7 oxygen atoms per Pt atom present or $PtO_{1.7}$. This is suggestive of PtO_2, which is the form of platinum oxide formed upon interaction of both molecular oxygen and oxygen atoms with Pt (*38*), and also suggests that for these small Pt crystallites the entire crystallite underwent oxidation.

H_2 titration of the deactivated unsintered Pt catalyst yielded 5.6 hydrogen atoms taken up per surface Pt atom. This is not consistent with the typical stoichiometry of hydrogen–oxygen titration, $3H + Pt\text{–}O \rightarrow H_2O + Pt\text{–}H$; it is more consistent with



$$6H + Pt\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix} \rightarrow 2H_2O + Pt\text{—}H.$$

This suggests, a surface composition consistent with PtO_2, in accord with the suggested bulk composition from the higher-temperature NH_3 reduction results.

The amount of N_2 evolved over a period of 1 hr after substracting off the amount evolved during the first 5 min in a similar experiment with the sintered Pt catalyst was about 0.8×10^{-5} g-moles N_2/g catalyst, which indicates 2.4×10^{-5} g-atom of O/g catalyst using the same stoichiometry as above. The sintered Pt catalyst contained 0.34×10^{-5} g-atoms of surface Pt atoms per gram of catalyst. Thus, there were about seven oxygen atoms per surface Pt atom present or about 0.5 oxygen atoms per Pt atom in the crystallites.

This indicates that the large (155 Å) Pt crystallites were not completely oxidized as were the small ones and that only the surface, about three or four Pt layers deep, underwent oxidation. This would explain the twofold larger extent of deactivation for the smaller crystallites (Table 1). Freel (*39*) has also suggested that supported Pt metal crystallites can undergo bulk oxidation. Our results are also in accord with the observation of Mitrofanova, Boronin, and Poltorak (*3,5*) that small Pt crystallites are more susceptible to oxidation than larger ones. Lundquist and Stonehart (*40*) have observed more than monolayer oxidation of Pt surfaces and have observed that the rate of oxide formation and reduction is dependent on Pt crystallite size in electrochemical studies.

CONCLUSIONS

The deactivation of supported Pt observed in low-temperature NH_3 oxidation is due to an oxidation of the Pt crystallites to the extent of at least several atomic layers in depth. This represents almost complete oxidation of the small Pt crystallites. The deactivation process requires reaction between NH_3 and O_2 to produce either a sufficiently excited oxygen atom or sufficient local heating to induce the Pt–oxygen reaction, since no deactivation is caused by either reactant singly. The surface oxide formed is much different and much less reactive than is chemisorbed oxygen on Pt. The deactivation can be completely reversed by a process which will remove the oxide.

Oxide formation introduces a variability into the surface properties of platinum, and undoubtedly other precious metals during oxidation reactions, that makes the catalytic activity respond slowly to changes in the gas-phase composition (*9,10*) and makes reproducing catalytic activity difficult (*41*). It can also contribute as a secondary crystallite size effect over and above primary crystallite size effects present in the supported Pt systems (*4,5*). This observed surface oxidation suggests that oxidation reactions over noble metals may involve more a metal oxide surface than a noble metal surface; i.e., in oxidation reactions noble metals may not be as noble as normally assumed.

NOMENCLATURE

k_D	Rate constant for rate decay
k_S	Surface reaction rate constant including all kinetic parameters
M_1	Initial rate, sec^{-1}
M_2	Time constant for rate decay, seconds
N	Density of active surface sites, number of sites/cm^2
N_0	Initial density of active sites, number of sites/cm^2
r	Observed rate of reaction, sec^{-1}
r_{ss}	Steady-state rate of reaction, sec^{-1}
t	Time, seconds

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