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SO_2 Deactivation in NO Reduction by NH_3

IV. Auger Studies of Deactivated Catalysts in Selective NO Reduction

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Deactivation of supported metal catalysts by SO_2 in the selective reduction of NO by NH_3 was studied in a differential, packed-bed flow reactor as a function of the gas-phase O_2 concentration, and foils of the same metal as the catalyst were placed in the reactor with the catalyst. Auger electron spectroscopy (AES) was used to analyze the metal foils subsequent to reaction. With no SO_2 in the feed gas, the rate of NO reduction over Pt/Al_2O_3, Ru/Al_2O_3, and Ni/Al_2O_3 was enhanced by the presence of 0.5 mole% O_2, whereas that for Pd/Al_2O_3 was reduced. AES studies confirm that the deactivation of Pd in the sulfur-free system is due to oxidation of the metal. Although SO_2 severely poisons the catalytic activity in the $NO–NH_3–SO_2$ system, addition of 0.5 mole% O_2 to the feed gas largely restores the activity of all catalysts. This elimination of severe SO_2 deactivation correlates well with the incorporation of oxygen to high concentrations into the subsurface layers of the metal; oxygen appears to counteract the presence of sulfur incorporation. Only metal oxides and metal sulfides were formed; there was no evidence of sulfate formation.

INTRODUCTION

Catalytic NO_X reduction over supported metals is an important means of meeting emission limits on NO_X from both mobile and stationary sources. Yet most exhaust and flue gases contain SO_2, which under reducing conditions is a severe catalyst poison (*1–6*), apparently due to the formation of extremely stable metal sulfides. However, under oxidizing conditions some metals are not affected by SO_2 or other sulfur-containing compounds. Pt is an excellent catalyst for oxidizing SO_2 and SO_3 (*7*), and SO_2 does not poison precious metal catalysts during CO and hydrocarbon oxidation (*3, 4*). In contrast, base metal oxides are poisoned by sulfur compounds, presumably due to stable metal sulfate formation under strongly oxidizing conditions.

Most exhaust and flue gas streams contain from 1 to 5% O_2. With a nonselective reducing agent, O_2 is reduced before the NO_X is reduced requiring much reductant, and the O_2 concentration varies markedly through the reactor. In the three-way catalytic muffler the feed gas mixture is approximately stoichiometric, and the O_2 concentration varies from several percent to zero. The effect of sulfur compounds (SO_2) on catalytic behavior in systems that are not strongly oxidizing or reducing has not been investigated; yet it is very important.

Ammonia and H_2 will selectively reduce NO without appreciably reducing the O_2 (*8–11*), allowing the oxidation potential of the gas stream to be varied without grossly affecting the surface-catalyzed NO reduction reaction. The gas-phase oxidation potential should affect the extent and nature of poisoning by SO_2. Thus the selective reduction system allows SO_2 to be used as a probe of the microenvironment on the sur-

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face of the catalyst as a function of gas-phase composition. A reducing microenvironment would be expected to result in severe poisoning by SO_2; whereas an oxidizing microenvironment would be expected to lead to a less severe poisoning by SO_2 or protection of surface activity from SO_2 poisoning.

The purpose of this study was to determine the extent and cause of deactivation of supported metal catalysts by SO_2 in the selective reduction of NO by NH_3 as a function of the gas-phase O_2 concentration. Foils of the appropriate metal were placed in the reactor with supported metal catalyst and were retrieved after steady-state operation to determine the surface composition and the concentration–depth profile of elements using Auger electron spectroscopy (AES).

EXPERIMENTAL METHODS

Apparatus

A packed-bed, continuous-flow microreactor was used to obtain the data. Apparatus and procedure were essentially the same as described earlier (*12*); only differences will be briefly described. Nitric oxide, O_2, and NH_3 (premixed in He) were mixed with He to give the desired feed composition. The reactor was immersed in a fluidized sand bath (±1°C); a thermocouple in the catalyst bed demonstrated equality of bath and reactor temperature. Exit gas from the reactor was injected into a dual-column gas chromatograph, so that the instantaneous rate of reaction could be determined as a function of on-stream time. The O_2-containing gas stream was mixed with the other gases just before the reactor entrance to reduce the residence time of O_2 with NO, minimizing the extent of NO_2 formation by homogeneous reaction; NO_2 reacts homogeneously with NH_3 forming N_2 and NH_4NO_2 (*13*). Immediately following the reactor, a U-tube immersed in liquid nitrogen was used to trap out NO and NH_3 to minimize the homogeneous formation of N_2 in the lines leading to the gas chromatograph and in the gas chromatograph column.

Metal foils were analyzed by AES after reaction. The spectrometer contained an Ar^+ gun to allow ion etching to obtain concentration–depth profiles.

Procedure

The procedure has been adequately described by Tsai *et al.* (*12*), and is summarized here. From 0.5 to 1.0 g of catalyst was loaded into the reactor between two glass-wool plugs, and a piece of foil was placed on top of the upper glass-wool plug. All catalysts and foils were reduced with H_2 (150 cm^3/min) at 250°C, except nickel, which was reduced at 450°C. Gas flow rates were set to give typically 1.0% NO, 1.0% NH_3, 0.5% O_2, and 50 ppm SO_2 (except for a series of SO_2-free runs) in He. Gas flow rate was set such that conversion of limiting reactant was typically below 10%, and differential operation was confirmed. Samples were taken periodically to follow transients, and steady state was typically achieved in 15 hr; runs were typically carried out for 24 or 48 hr to allow the metal foils to approach steady state under reaction conditions.

To minimize the effect of shutdown on the surface composition, the reactor was removed rapidly from the sandbath with reactions flowing and cooled quickly. The foil were contacted with air slowly and were stored in glass vials under He until they could be loaded into the Auger electron spectrometer for analysis. First the surface composition of each foil was determined by AES; each foil was then Ar^+ etched to obtain composition–depth profiles (*12*). For Pt metal the sputtering rate at standard operating conditions was about 20 Å/min; the actual sputtering rate for oxide or sulfide surfaces may have been considerably lower.

Analytical Methods

Analysis was by gas chromatography (*12*). Dinitrogen formation rates were determined with the U-tube behind the reactor immersed in liquid nitrogen to reduce homogeneous N_2 formation. The system was calibrated for homogeneous N_2 formation rates, which represented less than 10% of the total N_2 formation rate. This was subtracted from the measured N_2 formation rates. Nitrous oxide formation rates were determined without complications.

Materials Used

All gases used were research-grade (highest purity) gases in high-purity helium. Pt/Al_2O_3, Pd/Al_2O_3, and Ru/Al_2O_3 were all from Engelhard and contained 0.5 wt% metal; Ni/Al_2O_3 was from Harshaw (Ni-0301) and contained 11.0 wt% nickel (*12*). The Pt/Al_2O_3 catalyst had an average crystallite diameter of 43 Å. The Ni/Al_2O_3 had Ni crystallites averaging about 50 Å as determined by X-ray line broadening. The dispersion of the other catalysts was about equally high.

The metal foils were all better than 99.9% pure and were obtained from Alpha, with the exception of Ru which was produced by powder metallurgy by INCO. Except for Ru, they were cleaned by oxidation in flowing O_2 at 650°C for 2 to 18 hr, and were reduced for 3 hr in flowing H_2 at 550°C (*12*). Ru was cleaned by oxidation with nitric acid (*12*).

RESULTS

CATALYTIC ACTIVITY

NO–NH_3–O_2 system. The catalytic activity of each of the supported metals for the selective reduction of NO was determined using a feed of 1% NO, 1% NH_3, and 0.5% O_2 in He at 200°C (Table 1). The reproducibility of the N_2O formation rate was ±10%; that of the N_2 formation rate was about ±20% because of the homogeneous formation of N_2. In contrast to the situation in the absence of O_2, in which a 2- to 3-fold reduction in activity occurred before steady-state activity was reached, there was less than a 5% loss in activity with 0.5% O_2 in the feed gas stream between 3 and 1200 min on-stream time for Pt/Al_2O_3 and Pd/Al_2O_3. On the other hand in the presence of 0.5% O_2 the activity of Ru/Al_2O_3 decreased about 4-fold, and Ni/Al_2O_3 underwent an 8.5-fold decrease from initial activity to steady-state activity.

The steady-state rate of NO reduction over Pt/Al_2O_3 is enhanced about 20-fold over that for the NO–NH_3 system by 0.5 mole% O_2 in the feed gas; a similar increase upon O_2 addition has been reported by Pusateri *et al.* (*11*) and by Markvart and Pour (*14*). The rate for Pd/Al_2O_3 on the

TABLE 1

Steady-State Rates in NO Reduction by NH_3[a]

Catalyst	O_2 concentration[b] (mole%)	N_2 rate[c] (×10^4)	N_2O rate[c] (×10^4)	Selectivity, r_{N_2}/r_{N_2O}	Total product[d] formation rate (×10^4)
0.5% Pt/Al_2O_3	0.0	12.3	5.8	2.1	18.1
	0.5	~250	~240	1.0	490.0
0.5% Pd/Al_2O_3	0.0	10.0	6.2	1.8	16.2
	0.5	6.2	0.89	7.0	7.1
0.5% Ru/Al_2O_3	0.0	0.10	0.06	1.7	0.16
	0.5	0.44	0.16	2.75	0.60
11% Ni/Al_2O_3	0.0	0.09	0.05	1.8	0.14
	0.5	0.56	0.13	4.3	0.69

[a] Reaction conditions: 200°C (Pd, 203°C), 1 atm total pressure, 1% NO, and 1% NH_3 in He.

[b] Values for 0.0% O_2 are from Foley *et al.* (*1*).

[c] g-mole/g-cat-hr.

[d] Sum of N_2O and N_2 rates.

other hand was about 40% lower for 0.5 mole% O_2 in agreement with Markvart and Pour (*14*). Ru/Al_2O_3 and Ni/Al_2O_3 underwent about 4-fold and 6-fold rate increases, respectively, with the introduction of 0.5 mole% O_2 into the feed gas.

NO-NH_3-O_2-SO_2 System

The effect of SO_2 on catalytic behavior was studied with 50 ppm SO_2 in 1% NO, 1% NH_3, and 0.5% O_2 in He at 200°C. Runs were started without SO_2, and when steady-state activity was reached, 50 ppm SO_2 was added to the feed gas stream, and the new steady-state activity was determined (Table 2). With the exception of Pd, the steady-state NO reduction activity of the catalysts in the NO–NH_3–O_2–SO_2 system was essentially the same as that in the NO–NH_3 system. The activity of Pd with SO_2 and O_2 was one-thirtieth of that in their absence but was still several orders of magnitude greater than that in the NO–NH_3–SO_2 system (*12*). For Ni/Al_2O_3 and Ru/Al_2O_3 the rate was even higher than in the absence of SO_2 and O_2. For Pt/Al_2O_3, Pd/Al_2O_3, and Ni/Al_2O_3 the difference in activity upon the addition of O_2 to the NO–NH_3–SO_2 system was equivalent to about a 280°C temperature increase or about a four orders of magnitude rate increase. Although NH_3 selectively reduces NO in the presence of O_2, the microenvironment at the surface of the metal appears to be sufficiently oxidizing in the presence of O_2 that SO_2 deactivation was largely eliminated.

TABLE 2

Steady-State Activity in Selective Reduction of NO in the Presence of SO_2[a]

Catalyst	N_2 rate[b] ($\times 10^4$)	N_2O rate[b] ($\times 10^4$)	r_{N_2}/r_{N_2O}
0.5% Pt/Al_2O_3	10.0	7.1	1.4
0.5% Pd/Al_2O_3	0.44	0.10	4.4
0.5% Ru/Al_2O_3	0.26	0.031	8.4
11% Ni/Al_2O_3	0.13	0.015	8.7

[a] Reaction Conditions: 200°C, 1 atm total pressure, 1% NO, 1% NH_3, 0.5% O_2, and 50 ppm SO_2 in He.

[b] Rate in g-mole/g-cat-hr.

AES ANALYSES OF METAL FOILS

General

The applicability and validity of analyzing foils placed in a catalyst bed have been discussed previously (*12, 15*). Transfer through the atmosphere results in oxygen adsorption on the surface; however, earlier work (*12, 16, 17*) has shown that, with the exception of Ni, contact with O_2 at ambient conditions results in little removal of sulfur and carbon from the surface and no change in the subsurface composition. Nickel is so readily oxidized that multilayer oxide can form if the surface is not first passivated by O_2; this oxidation removes little sulfur but forms oxide over the sulfur (*17*). Blank runs using identical conditions but without reaction were made to account for the effect of pretreatment, reduction, and atmospheric transfer. The differences in spectra between the blank runs and those after reaction are considered to result only from reaction. For all systems except the NO–NH_3–SO_2 system the reaction temperature was 200°C. For NO–NH_3–SO_2 system the reaction temperature was 400°C for Pt/Al_2O_3, Pd/Al_2O_3, and Ni/Al_2O_3; for Ru/Al_2O_3 the reaction temperature was 250°C.

Below comparisons are made among metals exposed to the same reaction conditions in terms of intensities of oxygen and sulfur peaks measured under identical spectrometer conditions Reproducibility between runs is demonstrated for two independent runs with Pt in the NO–NH_3–O_2 system:

Sputtering time (min)	O(510):Pt(64) Peak ratio	
	Run 1	Run 2
0.0	0.22	0.35
1.0	0.06	0.05
1.5	—	0.03
2.5	0.05	—

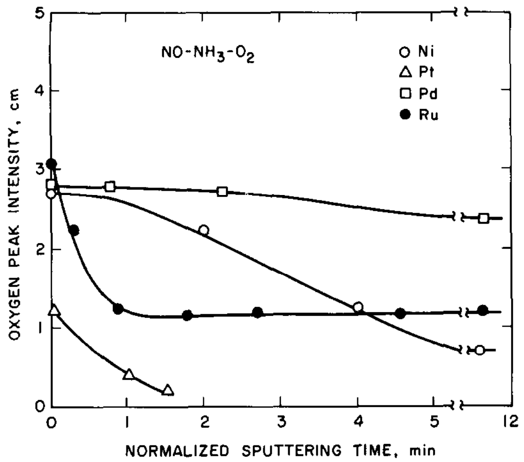

FIG. 1. Oxygen peak intensities as a function of normalized sputtering time for metal foils after deactivation under 1% NO, 1% NH_3, and 0.5% O_2 in He at 200°C.

NO–NH_3–O_2 System

Platinum. The AES spectrum of the Pt foil exhibited an intense oxygen peak (1.3 cm, Fig. 1) and a weak nitrogen peak, which represented less than 10% of a monolayer of nitrogen atoms. The nitrogen peak rapidly sputtered to zero. Sputtering reduced the intensity of the oxygen peak to zero as rapidly as for the blank runs.

Palladium. Palladium foil exhibited a strong surface oxygen peak (2.8 cm, Fig. 1) and a weak nitrogen peak, which rapidly sputtered to zero. The oxygen peak intensity did not decrease with sputtering time indicating that the Pd had undergone bulk oxidation during reaction. Pd is the only metal that showed such extensive incorporation of oxygen into the bulk. The lower steady-state activity of Pd in the NO–NH_3-O_2 system as compared with the NO–NH_3 system is due to the fact that Pd becomes oxidized and the other metals do not.

Ruthenium. An intense surface oxygen peak (3.0 cm) and a nitrogen peak were present in the spectrum of the Ru foil. The nitrogen peak intensity was the same as that found for the NO–NH_3 and NO–NH_3–SO_2 systems (*12*) and was considerably stronger than that for the other metals. Sputtering rapidly eliminated the nitrogen peak. The oxygen peak intensity was reduced more slowly and reached a constant value which was higher than the blank background value after 1 min of sputtering (Fig. 1).

Nickel. Nickel foil underwent extensive oxidation in the near-surface regions (peak intensity = 2.8 cm) as had been observed previously (*16*). Upon sputtering the oxygen peak decreased to a low constant value (Fig. 1).

NO–NH_3–O_2–SO_2 System

Platinum. The surface of the platinum foil contained a strong peak (1.6 cm, Fig. 2) and a several-fold more intense sulfur peak (3.55 cm, Fig. 3). Upon sputtering the oxygen peak intensity decreased only slightly and remained constant (~1.45 cm) with long-term sputtering (Fig. 2), whereas the sulfur peak intensity decreased sharply with sputtering (Fig. 3). This represents the most extensive incorporation of oxygen into the bulk of Pt observed for any system studied and is not achievable in the presence of O_2 alone. For the sulfur, there was a peak with a shape characteristic of metal sulfide at 150 eV (*12, 16, 17*); there was no evidence for adsorbed SO_X species.

Palladium. The Pd foil showed intense

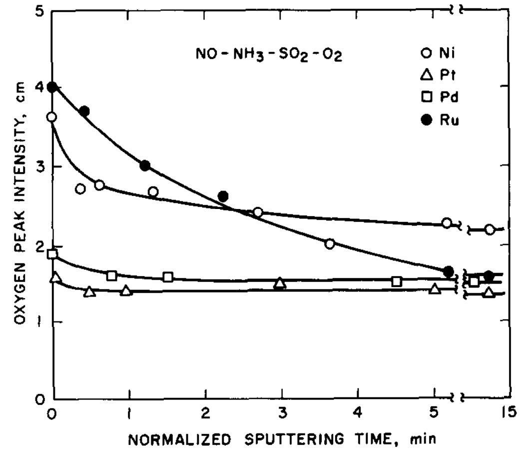

FIG. 2. Oxygen peak intensities as a function of normalized sputtering time for metal foils after deactivation under 1% NO, 1% NH_3, 0.50% O_2, and 250 ppm SO_2 in He at 200°C.

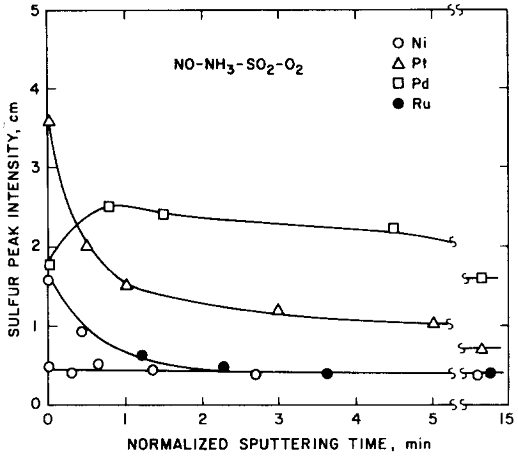

FIG. 3. Sulfur peak intensity as a function of normalized sputtering time for metal foils after deactivation under 1% NO, 1% NH_3, 0.50% O_2, and 250 ppm SO_2 in He at 200°C.

surface sulfur (1.8 cm, Fig. 2) and oxygen (1.9 cm, Fig. 3) peaks in its AES spectrum. As with Pt, the oxygen peak intensity decreased slightly upon sputtering, whereas the change in sulfur peak intensity was more complex. An initial increase in peak intensity probably caused by removal of surface oxygen picked up during transfer was followed by a slow decrease. The sulfur peak shape was characteristic of sulfide sulfur.

Ruthenium. The Ru foil showed a weak nitrogen peak and a strong oxygen peak (4.0 cm, Fig. 2). The sulfur peak intensity (1.6 cm) was somewhat less than for Pt and Pd foils (Fig. 3). Sputtering eliminated the nitrogen peak immediately and rapidly reduced the sulfur peak intensity to a low value (0.4 cm). The oxygen peak was reduced less rapidly than the sulfur peak and leveled off at a value (1.8 cm) four times the peak intensity for sulfur. The peak shape was characteristic of metal sulfide.

Nickel. The surface of the Ni foil was predominantly covered with oxygen (3.6 cm, Fig. 2), with a trace of sulfur (0.4 cm, Fig. 3). The oxygen peak intensity decreased to a constant value (2.2 cm) upon sputtering, whereas the sulfur peak intensity remained unchanged. The original peak intensity for oxygen is two-thirds of that for nickel oxide; that for sulfur is much less (approximately one-tenth) than that of nickel sulfide.

DISCUSSION OF RESULTS

COMPARISON OF REACTION SYSTEMS

Below, the behavior of each metal will be compared for the complete set of reaction systems studied including the O_2-free systems presented earlier (*12*).

Platinum

Sulfur-free system. Figure 4 gives the oxygen (510 eV) to platinum (64 eV) peak ratio as a function of normalized sputtering time for all the NO reduction systems studied. Taking the ratio of peaks removes all variations in instrument operating parameters and is the most precise method of comparing data. The activity for NO reduction by NH_3 increases markedly in the presence of O_2 (Table 1). Figure 4 shows that both surface and subsurface layers have *less* oxygen for the NO–NH_3–O_2 system than for the NO–NH_3 system. Repeat runs

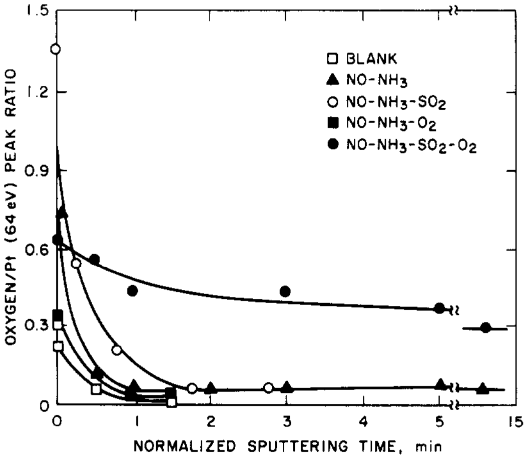

FIG. 4. Oxygen to platinum peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3; the blank shows the effect of *in situ* reduction and transfer to the Auger chamber. Reaction conditions: 1.0 vol% NO, 1.0 vol% NH_3, 0.50 vol% O_2, and 250 ppm SO_2 in He when the latter two components were present; reaction temperature was 200°C except for the NO–NH_3–SO_2 system for which the temperature was 400°C.

gave the same results. This supports the view that Pt catalyst deactivation in the NO–NH_3 system is the result of Pt surface oxidation (*18*); the AES studies show more oxygen incorporation with the NO–NH_3 system than with the NO–NH_3–O_2 system, where deactivation does not occur (*11*). The enhanced activity in the presence of O_2 is qualitatively explained by the AES results. Since there is less oxygen incorporation into the catalyst with the NO–NH_3–O_2 system than with the NO–NH_3 system, more catalytic sites are available for NO reduction. Apparently the surface microenvironment is more reducing in the presence of O_2 than in its absence due to a change in the relative concentration of adsorbed species.

Added SO_2. Pt is severely poisoned by SO_2 (*12*) and shows marked recovery of activity upon addition of O_2 to the feed. The presence of SO_2 resulted in more oxygen being incorporated into Pt regardless of whether O_2 was present in the feed (Fig. 4); the surface microenvironment is more oxidizing in the presence of SO_2. In the presence of SO_2 alone, oxygen incorporation occurs only to a depth of the first few monolayers, even at 400°C. When both O_2 and SO_2 are present, oxygen is incorporated at a sixfold higher concentration to a much greater depth (Fig. 4), even at 200°C.

In spite of the extensive oxygen incorporation for the NO–NH_3–O_2–SO_2 system there is less surface oxygen with this system than in the NO–NH_3–SO_2 system. The high surface oxygen concentration for the NO–NH_3–SO_2 system is presumed to be caused by oxygen adsorbed during transfer, which is rapidly sputtered off the surface.

Sulfur incorporation in Pt for the NO–NH_3–SO_2 system was to the extent of several monolayers, with little change in sulfur intensity up to 1 min sputtering time (*12*), but oxygen was incorporated to a lesser extent since it had decreased to its background level by this time. The decrease in the S/Pt peak ratio up to 1 min sputtering time (Fig. 5) results from an increase in the Pt (64 eV) peak intensity due to a rapid reduction in the oxygen peak intensity with sputtering; the sulfur peak intensity remained essentially constant. For sputtering times longer than 1 min the sulfur peak intensity decreased rapidly toward zero (Fig. 5). For the NO–NH_3–O_2–SO_2 system there was less sulfur present on the surface (S peak intensity = 3.7 cm) than in the NO–NH_3–SO_2 system (S peak intensity = 5.8 cm); the higher S/Pt peak ratio for the surface in Fig. 5 is due to Pt peak intensity reduction caused by the oxygen present. The subsurface sulfur concentration for the NO–NH_3–O_2–SO_2 system is much less than that for the NO–NH_3–SO_2 system. For the NO–NH_3–O_2–SO_2 system the O/Pt peak ratio was 0.3 or greater for many monolayers into the bulk; this apparently kept sulfur from incorporating deep into the bulk. It is inferred that this oxygen incorporation reduces the concentration of sulfur in the surface and subsurface regions and thereby is responsible for preventing the severe activity loss observed in the NO–NH_3–SO_2 system.

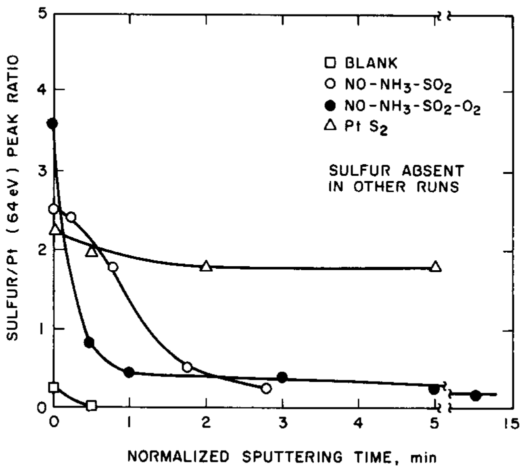

FIG. 5. Sulfur to platinum peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3; the blank shows the effect of *in situ* reduction and transfer to the Auger chamber. Reaction conditions are the same as given in Fig. 4.

A calibration standard of PtS_2 powder pressed into indium foil and sputtered is also shown in Fig. 5. This shows that the stoichiometry of the near-surface region in the case of the NO–NH_3–SO_2 system approaches that of PtS_2, indicating extensive sulfiding. Sulfur peaks were entirely of the sulfide form. This extent of sulfiding of Pt is very surprising in view of our observation that no sulfur incorporation into Pt foils was observed after 3 hr contact with 4 Torr H_2S in He at 250°C and with 4 Torr SO_2 in He at 350°C for 3 hr (*16*). Sputtering after both of the above treatments resulted in rapid (<30 sec) reduction of the sulfur peak intensity to zero. Reaction in the NO–NH_3–SO_2 system resulted in extensive sulfur incorporation which did not occur from either H_2S or SO_2 in the absence of reaction, indicating the important role of reaction in sulfur incorporation. We speculate that this reaction-induced incorporation of oxygen and sulfur is caused either by highly localized heat release due to reaction or by the formation of electronically excited Pt, O, or S atoms by reaction leading to oxidation or sulfiding of the subsurface regions, processes that are not possible in the absence of reaction.

Palladium

Sulfur-free system. Addition of O_2 to the NO–NH_3 system caused further deactivation of the Pd catalyst (Table 1). AES analysis (Fig. 6) showed that more oxygen is present on the surface and incorporated into the subsurface layers of Pd for the NO–NH_3–O_2 system than for the NO–NH_3 system. The deactivation of Pd caused by O_2 in the feed gas resulted from increased oxygen incorporation into the Pd, suggesting that activity reduction resulted from a change in the electronic properties and/or accessibility of surface Pd atoms. This is in contrast to Pt for which less oxygen was incorporated into the surface and subsurface layers for the NO–NH_3–O_2 system than for the NO–NH_3 system, resulting in significantly higher rates of reaction.

Added SO_2. The highest O/Pd peak ratio was observed for the NO–NH_3–SO_2 system. However, the oxygen peak intensity rapidly decreased upon sputtering becoming similar to or less than that for the NO–NH_3 system (Fig. 6). This high surface peak ratio suggests surface oxide. Introduction of O_2 with SO_2 resulted in significant incorporation of oxygen deep into the subsurface region of Pd; the level was about 30% lower than for the NO–NH_3–O_2 system. Oxidation of the Pd in the NO–NH_3–O_2 system reduced the NO reduction activity compared with that for the NO–NH_3 system. However, the bulk oxidation found in the NO–NH_3–O_2–SO_2 system is undoubtedly the reason that the extreme deactivation caused by SO_2 in the NO–NH_3–SO_2 system is largely eliminated in the NO–NH_3–O_2–SO_2 system.

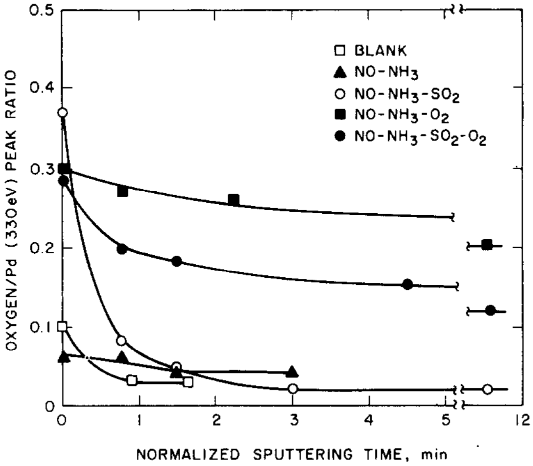

FIG. 6. Oxygen to palladium peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3; the blank shows the effect of *in situ* reduction and transfer to the Auger chamber. Reaction conditions are the same as given in Fig. 4.

There was extensive incorporation of sulfur into Pd, independent of the presence of O_2; in fact, the subsurface sulfur concentration was significantly greater in the NO–NH_3–O_2–SO_2 system than in the NO–NH_3–SO_2 system (Fig. 7). However, the sulfur peak intensities were considerably less than those for a stoichiometric sulfide. The maxima in the sulfur profiles near the surface (Fig. 7) resulted either from shadowing of sulfur by adsorbed oxygen,

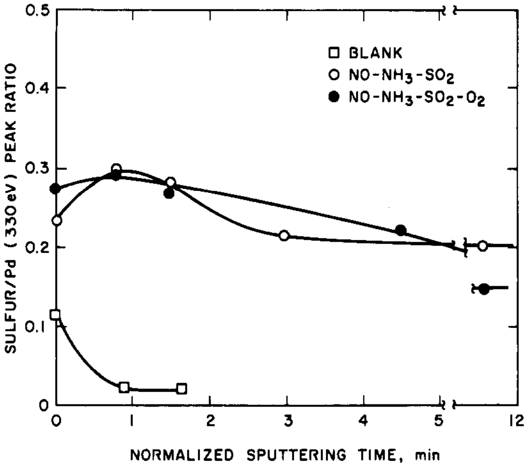

FIG. 7. Sulfur to palladium peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3; the blank shows the effect of *in situ* reduction and transfer to the Auger chamber. Raction conditions are the same as given in Fig. 4.

adsorbed SO_2, or from a slight removal of sulfur by O_2 during transfer. If it is due to removal in transfer, the effect is minor.

In sulfiding studies similar to those described for Pt involving either H_2S or SO_2 in He without reaction, the Pd foil underwent marked incorporation of sulfur from both H_2S and SO_2 (*12*). In contrast to Pt, where only a surface sulfide was formed under even the most severe treatment conditions, Pd was converted to bulk sulfide with the depth of the sulfide dependent on the temperature and time of contact. Four Torr SO_2 in He produced a Pd sulfide with a S/Pd (330 eV) peak ratio of 0.55, 4 Torr H_2S in He produced a Pd sulfide with a S/Pd (330 eV) peak ratio of 1.53. The S/Pd ratio appears to depend on the sulfiding activity of the sulfur-containing compound. Thus with 250 ppm (0.19 Torr) SO_2 in the reaction system the S/Pd ratio is smaller yet (S/Pd = 0.24, Fig. 7).

Ruthenium

Sulfur-free system. The Ru foil was made by powder metallurgy and thus may have contained some porosity. This may explain the background oxygen level for the Ru blank (Fig. 8). No oxidation of Ru occurred in the NO–NH_3 system. Addition of O_2 to the feed gas increased the NO reduction activity sixfold; the oxygen level on the surface increased significantly, but it remained unchanged in the bulk.

Added SO_2. There was a slight oxidation of the Ru surface with some incorporation of oxygen into the subsurface regions for the NO–NH_3–SO_2 and NO–NH_3–O_2 systems. Only for the NO–NH_3–O_2–SO_2 system was there extensive surface oxidation and incorporation of oxygen into the subsurface layers. The oxygen concentration (from peak intensities) near the surface is equivalent to that of nickel oxide (Fig. 2) indicating oxidation of the surface and near-surface region to essentially bulk ruthenium oxide.

For Ru in the NO–NH_3–SO_2 system the sulfur concentration was markedly lower than for the other metals (*12*). The presence of O_2 resulted in a threefold higher surface sulfur concentration with some incorporation into the subsurface region (Fig. 9). However, there was always much less sulfur than for Pt and Pd, and the concentration of oxygen was much higher than that of

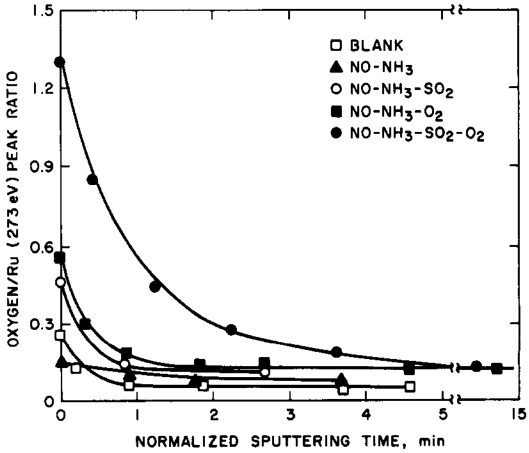

FIG. 8. Oxygen to ruthenium peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3; the blank shows the effect of *in situ* reduction and transfer to the Auger chamber. Reaction conditions are the same as given in Fig. 4.

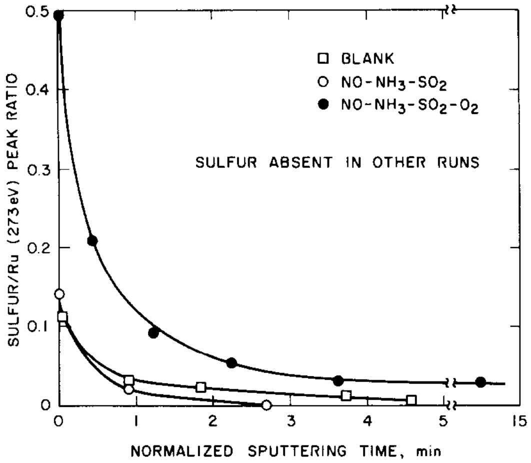

FIG. 9. Sulfur to ruthenium peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3; the blank shows the effect of *in situ* reduction and transfer to the Auger chamber. Reaction conditions are the same as given in Fig. 4.

sulfur. The lack of sulfur incorporation into Ru is clearly the reason that Ru is not severely deactivated by SO_2. This is apparently due to the inability of Ru to reduce SO_2 to S^{2-}, because H_2S poisoned Ru as extensively as Pt was poisoned by SO_2 and by H_2S in the absence of O_2 (*1*, *12*). During reduction of NO by H_2, Pt and Pd produced much NH_3 and in the presence of SO_2 produced H_2S; Ru produced almost no NH_3 and no detectable H_2S indicating its lower reducing activity (*1*). With H_2S in the feed gas, ruthenium sulfide is readily formed, and Ru is severely poisoned.

Nickel

Sulfur-free system. Addition of O_2 to the $NO–NH_3$ system slightly increased the bulk oxygen concentration (Fig. 10). Oxidation of the Ni foil is consistent with the observation that a well-reduced Ni/Al_2O_3 catalyst was converted to nickel oxide on Al_2O_3 after reaction in the $NO–NH_3$ system (*1*).

Added SO_2. For the $NO–NH_3–SO_2$ system, significantly more oxygen was incorporated into the bulk (Fig. 10). For the $NO–NH_3–O_2–SO_2$ system the amount of oxygen in the bulk was greater than for any of the other systems. The effect is more pronounced at greater depths where the O/Ni peak ratio with SO_2 was about five times the value without SO_2.

For the $NO–NH_3–SO_2$ system there was extensive sulfur incorporation into nickel giving a high value for the S/Ni peak ratio at a significant depth beneath the surface (Fig. 11). This high value is representative of nickel sulfide (*17*). This is about 27 times the amount of sulfur at the same depth for the $NO–NH_3–O_2–SO_2$ system. Added O_2 strongly inhibits sulfur incorporation into nickel and promotes oxygen incorporation into the bulk.

The sulfur depth profile for the $NO–NH_3–SO_2$ system is unusual in that the S/Ni peak ratio continuously increases with depth to a value of about 2.7. This is probably the result of oxidation of the Ni upon removing the sample from the reactor, forming a nickel oxide layer over the nickel sulfide. Similar sulfur profiles have been observed by Gould and Huss (*16*).

The addition of O_2 to the $NO–NH_3–SO_2$ system prevents sulfur incorporation and sulfide formation without significantly increasing oxygen incorporation. This may

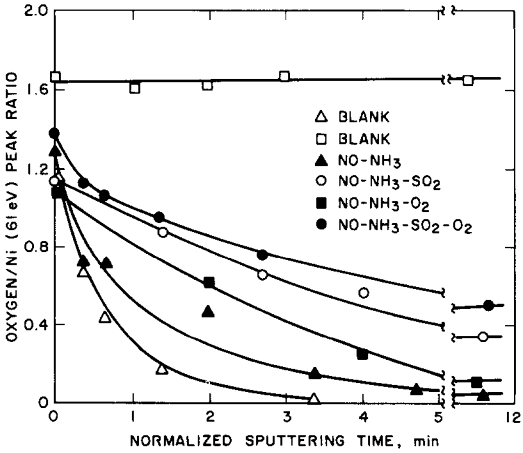

FIG. 10. Oxygen to nickel peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3: the blank shows the effect of *in situ* reduction and transfer into the Auger chamber. Reaction conditions are the same as given in Fig. 4.

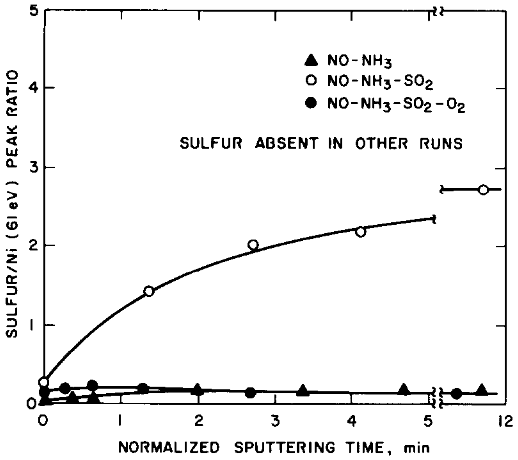

FIG. 11. Sulfur to nickel peak ratio of foils as a function of normalized sputtering time after deactivation in NO reduction by NH_3: the blank shows the effect of *in situ* reduction and transfer into the Auger chamber. Reaction conditions are the same as given in Fig. 4.

account for the high catalytic activity of Ni in the $NO-NH_3-O_2-SO_2$ system. The oxide is less active than the metal, but since all systems studied tend to oxidize the nickel, the observed rate is probably mainly affected by the extent of surface oxidation. The sulfide is much less active, and the observed activity in sulfur-containing systems is probably governed by the oxide–sulfide balance on the surface. This should be applicable to all metals in this study.

CORRELATION OF AES RESULTS WITH CATALYTIC BEHAVIOR

In the $NO-NH_3$ system the relative order of catalytic activity is (*1*, *12*)

$$Pt \approx Pd \gg Ru > Ni.$$

Pt and Pd were about 100-fold more active than Ru or Ni (Table 1). The high Ni content and small crystallite size of the Ni/Al_2O_3 indicate a significantly lower specific catalytic activity for Ni/Al_2O_3 than for Ru/Al_2O_3.

The AES results on the metal foils do not explain the activity differences of the metals; activity is an intrinsic property of the metal. The AES results confirm our earlier speculation (*11*) that the deactivation of Pt which occurs in the $NO-NH_3$ system is due to oxidation of the metal surface.

With 0.5% O_2 in the feed gas, the activity of Pt, Ru, and Ni increases, whereas that for Pd is reduced giving an activity order of

$$Pt \gg Pd > Ru > Ni.$$

The oxygen peak intensity on the surface was in the order

$$Ru, Pd, Ni > Pt.$$

The similarity is due to oxygen pickup during transfer. However, after sputtering briefly the order of decreasing oxygen peak intensity was

$$Pd > Ni \gg Ru > Pt.$$

The NO reduction activity correlates well with the inverse of the subsurface oxygen concentration; for Pd the exact order did not hold because of its much higher intrinsic activity, but its activity relative to Pt was reduced markedly with the observed oxygen incorporation.

The relative activity in the $NO-NH_3-SO_2$ system is (*12*)

$$Ru \ggg Pt, Pd, Ni.$$

The reduction of SO_2 to S^{2-} leading to the formation of metal sulfides results in severe deactivation for Pt, Pd, and Ni; whereas for Ru the absence of sulfide formation and the presence of a high oxygen concentration results in marked tolerance to SO_2. The AES studies thus correlate the catalytic activity with sulfur concentration.

The relative activity for the $NO-NH_3-O_2-SO_2$ system was

$$Pt \gg Pd, Ru > Ni,$$

and the severe deactivation caused by SO_2 was largely eliminated by the presence of O_2. This elimination of severe SO_2 deactivation correlates well with the incorporation of high oxygen concentrations into the metal subsurface regions; this implies that the surface oxygen concentration relative to sulfur was also high during reaction. The presence of surface and subsurface oxygen appears to counteract the presence of sulfur on the surface and in the subsurface regions.

These AES studies on metal foils in the reactor provide insight not otherwise available into the mechanism of sulfur deactivation and provide a relatively good interpretation of the differences in activity for different catalysts under different feed gas compositions. Since these results also correlate well with other behavior of these catalysts such as their activity for reduction of SO_2 to H_2S and of NO to NH_3 (*1*), there is considerable evidence that the results obtained for the foils can be extrapolated to the supported metals. However, until more quantitative information on the changes that occur for the supported metal catalysts can be developed, the extrapolation from foils to supported metals can be made no more quantitative.

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