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SO_2 Deactivation in NO Reduction by NH_3

III. Auger Studies of Deactivated Catalysts

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Deactivation of the supported metal catalysts by SO_2 in the reduction of NO by NH_3 was studied in a differential, packed-bed flow reactor. Foils of the same metals as the catalyst were placed in the reactor with the catalysts. Auger electron spectroscopy was used to study the metal foils subsequent to reaction. At 200°C, 50 ppm SO_2 reduced activity of Ru/Al_2O_3 by only fourfold as compared with three to five orders of magnitude activity reduction for Pt/Al_2O_3, Pd/Al_2O_3, and Ni/Al_2O_3. For Pt/Al_2O_3, Pd/Al_2O_3, and Ni/Al_2O_3, the surface of the metal foils was covered with approximately a monolayer of sulfur, and there was considerable incorporation of sulfur into the bulk of the metal. The Ru foil had a very small concentration of sulfur on the surface, and no sulfur was present in the subsurface layers. All of the sulfur present was in the form of sulfide; no sulfate was observed.

INTRODUCTION

The control of emissions of oxides in nitrogen (NO_X), which contribute to photochemical smog (*1*), has become increasingly important, and the catalytic chemistry of the reduction of NO_X is becoming increasingly well defined for several reductants (*2–6*). Reduction by NH_3 and by H_2 are of particular interest because they reduce NO_X selectively in the presence of high O_2 concentrations (*7–11*). Sulfur compounds, particularly SO_2 which is found in almost all gas streams containing NO_X, severely poison most NO_X reduction catalysts. Sulfur dioxide severely deactivates both Ni catalysts (*10, 12*) and noble metal catalysts (*10, 13–15*). Previous studies provide no mechanistic information on the poisoning of these metal catalysts by SO_2.

Sulfur dioxide rapidly adsorbs on Pt and Pd at −85°C, but sulfur is not incorporated into the metal at temperatures to 250°C (*16, 17*). Sulfur dioxide was incorporated into Ni above 100°C, but the chemical composition of the surface and near-surface layers was not determined (*18*). The interaction of SO_2 with Ni foils has been shown to produce nickel oxide layers rather than surface and near-surface layers containing sulfur (*3, 19*).

The purpose of this work was to determine the extent and cause of SO_2 deactivation of supported metal catalysts in NO reduction by NH_3. The work involved kinetic studies of SO_2 deactivation of supported metals. A foil of the appropriate metal was placed in the bed of particulate catalyst, was removed, and was examined by Auger electron spectroscopy (AES) after reaction to determine the surface composition and depth profile of elements into the metal foil. This allowed more direct interpretation of the sulfur-poisoning mechanism.

EXPERIMENTAL

Apparatus

A packed-bed, continuous-plug-flow, microreactor connected to two on-line gas

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chromatographs was used for these studies. Nitric oxide, SO_2, and NH_3 (all premixed in He) were mixed with He to give the desired feed composition. Helium was passed over a heated, reduced copper catalyst to remove O_2, mixed with a He/NO stream, and passed over molecular sieves to remove H_2O. Sulfur dioxide in He and NH_3 in He were added to the stream just before the reactor. All lines were 316 stainless steel. Because O_2 affects the reaction significantly, the system was rigorously checked for leaks prior to each run. The reactor consisted of a 50 × 1.27-cm Pyrex of quartz tube (Fig. 1) held in a stainless-steel block in a Lindburg furnace. Supported metal catalyst and metal foils were placed in the center of the tube between glass-wool plugs with a thermocouple in the catalyst bed. The exit gas was injected directly into two gas chromatographs in parallel for analysis; all components could be determined. The instantaneous reaction rate was measured as a function of on-stream time.

Auger electron spectroscopy (AES, Physical Electronics Industries) was used to examine the foils after reaction. The spectrometer contained an ion gun to allow argon ion etching to obtain concentration–depth profiles.

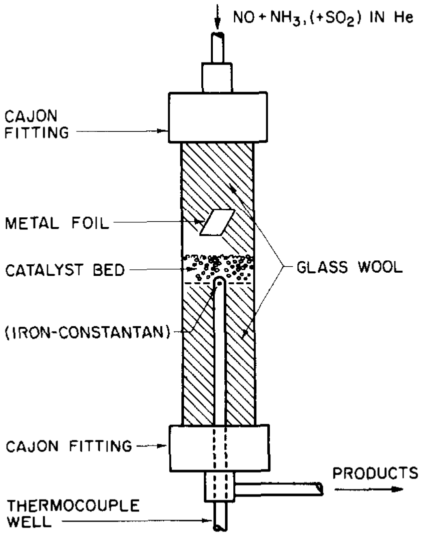

FIG. 1. Diagram of the reactor assembly showing placement of catalyst and metal foil.

Procedure

Typically, 0.5 to 1.0 g of catalyst was loaded into the reactor between two glass-wool plugs with a thermocouple in the catalyst bed. The reactor was put into the furnace, the system was leak tested, and the gas flow rates were set to give differential conversion (<20% conv.) with typically 1.0% NO, 1.0% NH_3 in He. SO_2 (50 ppm) was added to the feed during poisoning studies.

In a parallel set of experiments, a piece of foil (1.0 × 0.5 cm) of the appropriate metal was placed vertically on top of the glass wool. Runs in which the foil was placed directly in the catalyst bed gave the same results. Catalyst and foil were reduced with H_2 (150 cm^3/min) at 250°C for all catalysts, except Ni/Al_2O_3 which was reduced at 450°C. Hydrogen reduction in the reactor had no effect on the final steady-state activity observed. Samples were taken periodically to follow transients, and steady-state activities were determined. Steady state was typically achieved in 15 hr; runs were typically continued for 24 hr. Lower SO_2 concentrations required longer times to achieve steady state. Rates of reaction were calculated in terms of N_2 and N_2O formed; N_2 and N_2O are the primary products of NO reduction by NH_3 (*20*).

Sulfur dioxide adsorbed on tubing upstream of the reactor caused poisoning in subsequent "SO_2-free" runs. To eliminate this "back-poisoning," all lines which had been exposed to SO_2 were purged with He while slowly working from the upstream to the downstream end of each line with a heat gun. Several cycles of this treatment over an hour eliminated sulfur poisoning, giving rates that were equivalent to those obtained by Pusateri *et al.* (*11*), prior to introducing any sulfur compounds into the system.

Because of the need to avoid any changes in the surface composition of the foils from their steady-state composition during shutdown and because of our previous observation that the surfaces were oxidized under the reaction conditions used here (*11*), shutdown involving opening the oven, shutting off the NH_3–He feed gas, and removing the reactor tube from the metal sheath as soon as it was cool. The foils were slowly contacted with air, and were stored in glass vials under He until they could be loaded into the AES vacuum chamber for analysis. Transfer procedures used here have been shown to introduce no substantial changes in the foils other than adsorption of oxygen on their surfaces, with the exception of Ni (*19*).

Foils were loaded onto a carousel sample holder in the main chamber of the Auger electron spectrometer. An initial AES scan was taken from 0 to 1900 eV to determine the surface composition of each foil, and peaks of interest were remeasured more carefully. Argon was then introduced into the system to a pressure of $\sim 5 \times 10^{-5}$ Torr, and the foil was sputtered for a predetermined length of time (a few seconds) at 1 kV, 10 mA emission current and 10 μA beam current. Sputtering was stopped, a full AES scan was taken, and the peaks of interest were remeasured. The sequence of sputtering and scanning was repeated until the oxygen and sulfur levels reached baseline or until it was evident that further changes could not occur upon continued sputtering.

Analytical Methods

All reactant and product species were separated and analyzed on parallel dual-column gas chromatographs. Nitrogen and NO were separated on a 2-m column of molecular sieve 5A (60–70 mesh); N_2O was separated from the other components on a 2-m column of Porapak Q, both at room temperature. Sulfur dioxide, H_2S, and N_2O were effectively separated on a 12-m × 0.318-cm-o.d. Teflon column packed with 5-ring polyphenyl ether/H_2PO_4 on 40/60-mesh Chromosorb T. Quantitative analysis was possible for SO_2 concentrations above 20 ppm.

AES peak intensities were determined by taking the distance between the maximum and minimum of the $d(N(E))/dE$ curve where $N(E)$ is the electron flux as a function of energy. These peak intensities were normalized to standard spectrometer operating conditions. Some peak intensities may have upward to 40% error due to spectrometer variations over an 8-month period, although in most cases the error is expected to be less.

Since the operating conditions of the Auger electron spectrometer changed from sample to sample, comparison of the ratio of peak intensities is better for determining the effects of different reaction environments on the same metal than is comparison of absolute peak intensities, since in taking the ratio the effect of all spectrometer operating parameters is minimized. However, the "peak ratio" method is not the best way to compare data from different metals since there are large variations in ionization cross sections and in Auger transition probabilities, and thus in characteristic metal peak intensity from one metal to another. Thus, the peak intensity for the same surface concentration of a species such as oxygen or sulfur, when divided by the metal peak intensity, gives different ratios for different metals. In the results presented here, absolute peak intensities normalized to standard spectrometer conditions are given. When several reaction conditions for the same metal are compared, the ratio of peaks is used; this is more precise in that variations in spectrometer operating parameters are minimized. The validity of these procedures and calibration standards is discussed elsewhere (*21*).

Depth profiles were obtained by sputtering with Ar^+ at constant beam current and ion gun voltage. Calculating the sputtering rate for pure metals is relatively straightforward; that for oxides and sulfides is not known, and may be as much as an order of magnitude less (*22*). In this work, all sputtering is given in terms of a *normalized sputtering time,* based on the sputtering yields for pure metal. This normalized sputtering time uses Pt as the standard at 1-kV gun voltage and 10-μA beam current and is defined as:

$$t_{N,i} = \frac{Y_{si}}{Y_{sPt}} \cdot t_i ,$$

where

$t_{N,i}$ = normalized sputtering time for metal i,
t_i = actual sputtering time for metal i,
Y_{si} = sputtering yield for metal i,
Y_{sPt} = sputtering yield for Pt.

For a comparison, equal normalized sputtering times for different metals should represent equal depth sputtered. Sputtering yields of 1.4, 2.1, 1.3, and 0.9 for Pt, Pd, Ru, and Ni, respectively, were used (*22*). The sputtering rate at operating conditions is about 20 Å/min for pure Pt metal.

Chemical shifts in the Auger peaks result from charge transfer to or from the atom, and peak shape changes occur whenever the electrons involved in the Auger process include valence electrons. Oxygen and sulfur are of particular interest here; metal oxide or sulfide formation could result in chemical shifts and peak shape changes. Colby (*23*) has shown that distinguishable differences in peak shapes exist between metal sulfides and metal sulfates, as shown in Fig. 2.

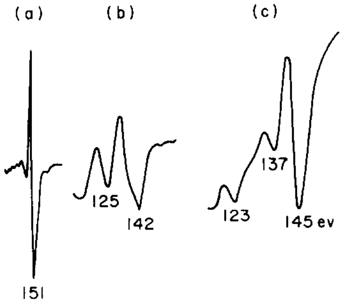

FIG. 2. AES peak shapes for nickel sulfide and for nickel sulfate. Sulfur as (a) nickel sulfide (*23*); nickel sulfate (*23*); sodium sulfate (*27*).

TABLE 1

Catalysts Used

Type	Metal loading (wt%)	Supplier
Pt/Al_2O_3	0.5	Englehard (Type M)
Pd/Al_2O_3	0.5	Englehard
Ru/Al_2O_3	0.5	Englehard
Ni/Al_2O_3 (Ni-0301)	11.0	Harshaw

Materials Used

All gases used were research grade (highest purity) mixed with high-purity He. Catalysts used are listed in Table 1. Catalysts were first crushed and screened to 28–60 mesh. They were cleaned by treating with O_2 (150 cm^3/min) while heating slowly to 450°C and holding at 450°C for 2 hr. They were then reduced in H_2 (150 cm^3/min) by heating slowly to 450°C and holding at 450°C for 2 hr, and were stored in glass bottles. The Pt/Al_2O_3 catalyst had a dispersion of 0.24 as determined by H_2 chemisorption, and 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 not determined, but they had about equally high dispersion.

The metal foils were cut into 1 × 0.5-cm pieces and were cleaned by a high-temperature oxidation–reduction cycle in a quartz tube as shown in Table 2. The foils were cooled in flowing H_2 and carefully passivated with air to avoid significant oxidation.

Oxidation of Pt foil at 450°C followed by reduction at 450°C produced a foil which contained only a small trace of sulfur, but carbon remained as the major contaminant; the 650°C treatment resulted in almost complete carbon removal (Fig. 3). After cleaning, Pd exhibited a small surface sulfur concentration; other impurities were not detectable. Brief sputtering showed that there were no detectable impurities immediately beneath the surface; similar results were

TABLE 2

Metal Foils

Metal	Foil thickness (mm)	Purity (%)	Treatment	Supplier
Pt	0.025	99.9	O_2 at 650°C, 18 hr; H_2 at 550°C, 3 hr	Alfa Products
Pd	0.025	99.9	O_2 at 650°C, 10 hr; H_2 at 550°C, 3 hr	Alfa Products
Ni	0.025	99.9	O_2 at 650°C, 2 hr; H_2 at 550°C, 3 hr	Alfa Products
Ru	0.038	High purity	HNO_3 (70%), 5 min; distilled water wash; air dry; H_2 at 400°C, 2 hr	INCO

obtained with nickel. Ruthenium foil was cleaned with concentrated nitric acid followed by H_2 reduction to avoid formation of toxic RuO_4 during an oxidation cycle. The as-received foil exhibited no impurities except carbon after H_2 reduction. Cleaning with nitric acid essentially eliminated the carbon from the surface.

RESULTS AND DISCUSSION

CATALYTIC ACTIVITY

NO–NH₃ System

Since most of the supported metals showed identical qualitative features for the reaction, only the results for Pt will be considered in detail; those of the other metals will be presented in summary form, except where behavior differed significantly. The kinetics associated with this system are presented elsewhere (*24*). In all cases, the catalytic activity declined by a factor of 2 to 4 from fresh catalyst activity to steady-state activity for both N_2 and N_2O formation. Table 3 gives the steady-state rates observed for each catalyst at 200°C. All rates were determined in the region of differential reactor operation (5 to 20% NO conversion) and reproducibility was demonstrated to be within ±10%. The value of 12.3×10^{-4} g-mole N_2/g-cat-hr for Pt/Al_2O_3 at 200°C agrees well with 11.6×10^{-4} g-mole N_2/g-cat-hr reported by Pusateri *et al.* (*11*) as does the selectivity to N_2.

Pt/Al_2O_3 and Pd/Al_2O_3 show similar activity in the absence of SO_2; Ru/Al_2O_3 and Ni/Al_2O_3 are about 100-fold less active (Table 3). Since all catalysts were highly dispersed (within a factor of 2), this may be considered to be the relative activity on a per unit metal surface area basis with the exception of Ni/Al_2O_3. Because of the high metal content of the Ni/Al_2O_3 catalyst and its high dispersion, the activity of the Ni/Al_2O_3 per unit metal surface area must be approximately one order of magnitude lower. This is the order observed by Markvart and Pour (*25*) for Pt/Al_2O_3, Pd/Al_2O_3, and Ru/Al_2O_3.

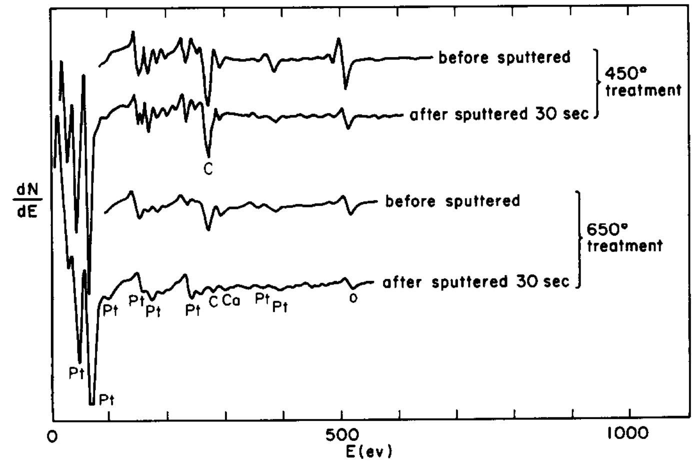

FIG. 3. AES spectra of platinum foil after 650°C O_2 treatment followed by reduction in H_2 at 550°C.

TABLE 3

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

Catalyst	Rate (g-mole/g-cat-hr)		Selectivity, r_{N_2}/r_{N_2O}
	$r_{N_2} \times 10^4$	$r_{N_2O} \times 10^4$	
0.5% Pt/Al_2O_3	12.3	6.0	2.05
0.5% Pd/Al_2O_3	10.0	6.2	1.6
0.5% Ru/Al_2O_3	0.10	0.06	1.7
11.0% Ni/Al_2O_3	0.09	0.05	1.8

[a] Reaction conditions: 200°C, 1.0% NO and 1.0% NH_3 in He, 1 atm total pressure.

The selectivity to N_2 was about 2.0 for all catalysts and agrees well with the selectivity observed by Pusateri *et al.* (*11*) and by Otto *et al.* (*20*) for Pt/Al_2O_3 and is also in accord with the selectivity predicted by the mechanism of NO reduction by NH_3 established by Otto *et al.* (*20*).

NO–NH_3–SO_2 System

The poisoning effect of SO_2 was so severe for Pt/Al_2O_3 that at 200°C and 50 ppm SO_2 no reaction could be detected; therefore, higher reaction temperatures were required to obtain measurable rates of reaction. The lowest temperature at which rates of reaction could be easily measured over Pt/Al_2O_3 was 400°C; this was chosen as the standard reaction temperature for catalysts not active enough at lower temperatures.

Figure 4 shows the effect of 250 ppm SO_2 in the feed gas on the rate of product formation over Pt/Al_2O_3 at 400°C. At on-stream times less than 20 min, conversion was 100%, and the rate of N_2 formation could not be calculated in this region. As steady state approached, conversion decreased to very low levels, and rates of N_2 and N_2O formation could be calculated accurately. For Pt/Al_2O_3 at 400°C with a feed gas containing 1% NO, 1% NH_3, and 250 ppm SO_2, the steady-state rates of N_2 and N_2O formation were less than 0.1×10^{-4} g-mole/g-cat-hr. For 50 ppm SO_2 in the feed gas, the steady-state rates were about 0.7×10^{-4} g-mole N_2/g-cat-hr and 0.2×10^{-4} g-mole N_2O/g-cat-hr (Table 4). Rates of NO reduction did not increase appreciably until the SO_2 concentration was reduced to 25 ppm or lower.

Both Pd/Al_2O_3 and Ni/Al_2O_3 underwent severe deactivation to give steady-state rates which were in the same range as that for Pt/Al_2O_3 for 50 ppm SO_2 and 400°C (Table 4).

Ru/Al_2O_3 was extremely resistant to SO_2 deactivation, giving complete conversion of NO at 400°C with 50 ppm SO_2 in the feed gas. At 233°C the rates of N_2 and N_2O formation were 3.8×10^{-4} g-mole N_2/g-cat-hr and 2.5×10^{-4} g-mole N_2O/g-cat-hr with 50 ppm SO_2 in the feed gas. When the rate of N_2 formation is extrapolated to 200°C using

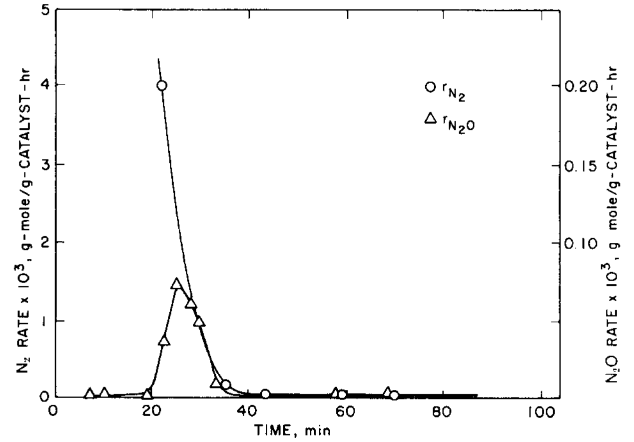

FIG. 4. Effect of SO_2 on rate of product formation catalyzed by Pt/Al_2O_3. Reaction conditions: 400°C, 1% NO, 1% NH_3, and 250 ppm SO_2 in He.

TABLE 4

Steady-State Rates of Reduction of NO by NH_3 in the Presence of 50 ppm SO_2[a]

Catalyst	Temperature (°C)	Rate (g-mole/g-cat-hr)		Selectivity, r_{N_2}/r_{N_2O}
		$r_{N_2} \times 10^4$	$r_{N_2O} \times 10^4$	
0.5% Pt/Al_2O_3	400	0.7[b]	0.2[b]	3.5
0.5% Pd/Al_2O_3	400	0.5	<0.1	>5
11.0% Ni/Al_2O_3	400	4.6	0.08	57
0.5% Ru/Al_2O_3	400	Complete conversion of NO		—
0.5% Ru/Al_2O_3	263	66.0	53.0	1.25

[a] Reaction conditions: 1.0% NO, 1.0% NH_3, and 50 ppm SO_2 in He, 1 atm total pressure.

[b] Extrapolated value.

the measured activation energy (*24*), the value is approximately one-fourth of that in the absence of SO_2. Extrapolation of the rates of N_2 formation for Pt/Al_2O_3 or Pd/Al_2O_3 in the presence of 50 ppm SO_2 to 200°C gives a value that is more than five orders of magnitude (10^{-5}) lower than that in the absence of SO_2. This comparison shows that Ru/Al_2O_3 is much more sulfur tolerant than the other metals studied. The studies on the supported metal catalysts alone do not provide sufficient reasons as to why Ru/Al_2O_3 behaves so differently from the other catalysts; other characterization is required.

SURFACE ANALYSIS OF METAL FOILS

General

Williams and Baron (*26*) have shown that useful information on the surfaces of aged catalysts can be obtained from metal foils inserted into catalyst beds. In the present work, metal foils were inserted into the reactor and thus were exposed to the same gas-phase environment as the supported metal catalyst. The surface area of each metal foil was small enough (~1 cm²) that it had a negligible effect on the measured conversion.

Because of exposure to the atmosphere during transfer from the reactor to the Auger electron spectrometer chamber, the surface composition of the foils may have been altered. However, previous studies (*19*) have shown that if contact with air is done slowly, by diffusive contact at room temperature, the surface composition is changed very little for the metals studied, with the exception of Ni; the major change that occurs is adsorption of oxygen on the surface.

Gould and Huss (*19*) showed that Pt and Pd foils which were cleaned and then sulfided with H_2S underwent little, if any, sulfur removal upon contact with the atmosphere at room temperature. No oxygen was found on the surface of well-sulfided samples after transfer through the atmosphere. They also showed that sulfided Ni foils are sensitive to oxygen, forming multilayer nickel oxide upon contact with oxygen at slightly elevated temperatures. Colby (*21, 23*) has shown that for Ni the formation of oxide occurs over the surface sulfur and that little sulfur is removed; the sulfur is buried under the nickel oxide that forms. Sputtering revealed the sulfur present originally when the oxide was sputtered away. These latter experiments were carried out in an antechamber attached to the main vacuum chamber of the Auger electron spectrometer so that transfer through the atmosphere was not involved.

The experimental procedure used here provides useful information on the surface concentration of species which relates to the catalytic behavior of the metal. It remains possible that in going from a mildly reducing environment (gas-phase condition) during reaction to an oxidizing environment in transfer through the atmosphere, some removal of surface species occurred. The differences in surface composition between metals and between reaction conditions suggest that surface compositional changes were not large. Even if surface changes were important, there is no evidence to suggest that transfer through the air could have had any effect on subsurface composition, with the exception of Ni. Thus, differences observed in sputtering profiles are the direct result of reaction-induced incorporation of species.

Blank Runs

A set of "blank" runs in which foils underwent the same pretreatment and treatment conditions including transfer through the atmosphere, but with the exception of reaction, were carried out to provide a baseline for interpretation of reaction results. After cleaning the foils were individually loaded into the reactor, reduced *in situ* for 1 hr at 250°C, cooled, contacted with air, removed, and then analyzed by AES. These foils were thus exposed to oxygen and other contaminants during transfer through the atmosphere, but they underwent no alterations due to reaction. The resultant surfaces, except for the Ni foil, showed small sulfur peaks and relatively small oxygen peaks. The sulfur was probably from the reactor system since it had been used for SO_2 deactivation studies prior to these experiments, and the sulfur represented at most 10% of a monolayer. The oxygen was adsorbed during transfer through the atmosphere. With the exception of Ni, the oxygen levels reduced to essentially zero after sputtering a few monolayers at most (Fig. 5). The low intensities of the oxygen peak (<1 cm) before sputtering and the rapid removal show that the oxygen is present only as a surface chemisorbed layer. The higher value of the oxygen peak intensity for Ni is representative of a bulk oxide forming with oxygen present on the surface and in subsurface layers. One of the blank Ni foils had undergone significant oxidation due to contact with the atmosphere upon removal from the reactor while the foil was still at an elevated temperature. The other foil, using the standard cool-down and air contact procedure, did not undergo oxidation (Fig. 5). Previous studies with Ni have shown that the temperature and rate of contact with oxygen are very important in determining the extent of oxidation (*19, 21*).

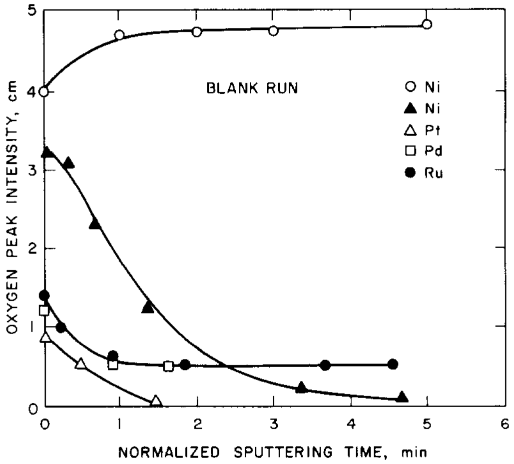

FIG. 5. Oxygen peak intensity as a function of normalized sputtering time for "blank run" metal foils at standard spectrometer conditions.

The reproducibility of the data for the NO–NH_3 system was checked by doing three runs with Pd. Surface oxygen levels varied significantly (0.06 to 0.26 for O/Pd (330 eV)), but the values of the O/Pd ratio after 0.75 min of sputtering were essentially the same at a value of 0.06 and decreased to a constant value of 0.03 after 3 min of sputtering.

Figure 6 shows the behavior of the sulfur peak intensity as a function of sputtering time for the blanks. Sulfur peaks were very small, indicative of a small fraction of a monolayer, and they were rapidly reduced to zero indicating surface sulfur only.

NO–NH_3 System

A series of NO reduction runs were carried out with metal foils in the reactor, and

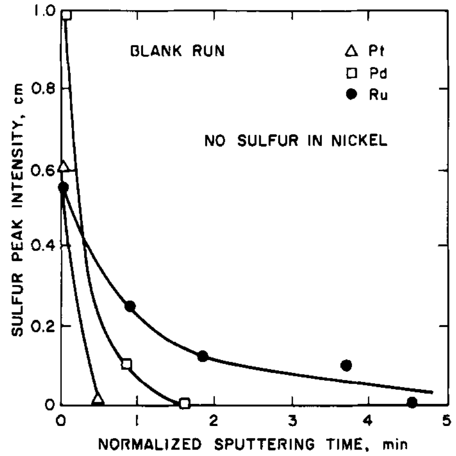

FIG. 6. Sulfur peak intensity as a function of normalized sputtering time for "blank run" metal foils at standard spectrometer conditions.

the runs were continued for at least twice the time required for the supported metal to reach steady-state activity to allow sufficient time for the surface and subsurface regions of the foil to reach a state representative of the steady-state condition of the surface and subsurface regions of the supported metal catalysts. The shutdown procedure involved stopping the NH_3 flow and cooling the sample as quickly as possible to reduce the effect of shutdown on the surface and subsurface regions.

Figure 7 shows the oxygen peak intensity at the surface and as a function of normalized sputtering time for the metal foils studied. After reaction the surface oxygen peak intensity is 1.5 cm for Pt (O/Pt = 0.75), 0.6 cm for Pd (O/Pd = 0.07), 1.0 cm for Ru (O/Ru = 0.16), and 2.7 cm for Ni (O/Ni = 1.3) (Fig. 7). The surface oxygen concentration for Pt is ~50% more after reaction than for the blank (O/Pt = 0.23 for the blank vs O/Pt = 0.75 after reaction). This indicates that an incomplete surface oxide was formed on Pt. Sputtering showed that there was considerable oxygen incorporated into the Pt subsurface regions. After 1 min of sputtering, there was no oxygen in the Pt blank; three repeat runs demonstrated this behavior. Oxygen was present in significant concentrations in the Pt sample after reaction following 5 min of sputtering (Fig. 7).

The increase in the subsurface oxygen intensity in Pt is most probably caused by incorporation of oxygen into the bulk due to reaction. Pd or Ru did not form any significant surface or bulk oxide, above that found for the blanks, during reaction in the NO–NH_3 system. For Pd the O/Pd (330 eV) peak ratio was 0.07 as compared with the O/Pd peak ratio of 0.29 for oxygen adsorbed on cleaned Pd (*19*). The oxygen concentration on the Ni "blank" was greater than 3.0 cm (O/Ni = 1.1 and 1.7). The blank which was contacted with ambient air using the standard procedure formed only a surface oxide. The AES spectrum of the Ni foil showed no elements other than oxygen and nickel. Sputtering for times up to 11 min resulted in a significant reduction in the oxygen and an increase in the nickel peak intensities, but no other elements appeared (Fig. 7). Clearly a deep nickel oxide layer had formed during reaction.

These results suggest that even in a stoichiometric excess of NH_3, the microenvironment at the surface of the catalyst, at least for Pt and Ni, is sufficiently oxidizing

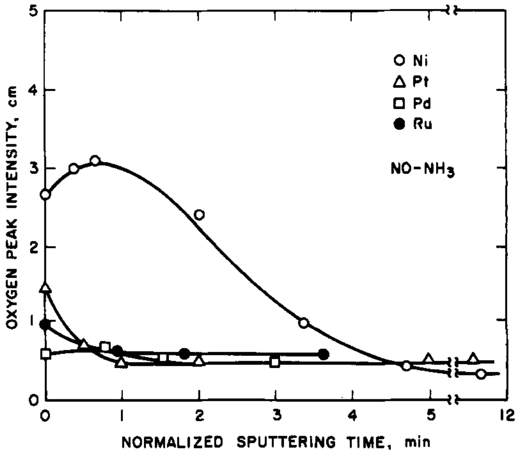

FIG. 7. Oxygen peak intensity as a function of normalized sputtering time for metal foils exposed to reaction. Reaction conditions: 200°C, 1% NO, and 1% NH_3 in He, 1 atm total pressure, run duration ~50 hr.

to have incorporated oxygen into subsurface layers.

The Pt, Pd, and Ru foils surfaces all contained significant nitrogen peaks which were not observed on blank samples. The nitrogen peak intensity was suggestive of as much as 10% of a monolayer on Pt and Ru.

NO-NH_3-SO_2 System

A series of NO reduction runs was carried out for 48 hr with a metal foil in the reactor using a feed gas of 1% NO, 1% NH_3, and 250 ppm SO_2 in He at 400°C. This is greater than 30 times the time required for the supported catalyst to achieve steady state. After reaction, the Pt surface contained very large sulfur and oxygen concentrations, and a small nitrogen concentration (Figs. 8 and 9). The oxygen and sulfur peak intensities decreased with sputtering, but the sulfur signal was reduced much more slowly than that of oxygen. Because there is a weak Pt peak at 150 eV which overlaps the sulfur peak at 151 eV, it is necessary to subtract the Pt peak contribution. This was done by first determining the Pt (150 eV) to Pt (64 eV) peak ratio for clean Pt (sputtered). The intensity of the Pt (151 eV) peak was then estimated by multiplying the Pt (64 eV) peak intensity by the ratio determined for clean Pt and then subtracting this intensity from that of the observed 151-eV peak to give the sulfur peak intensity. Figures 8 and 9 show the behavior of the oxygen and sulfur peak intensities as a function of normalized sputtering time. There is no evidence of changes in sulfur peak shape with sputtering the surface and subsurface layers away.

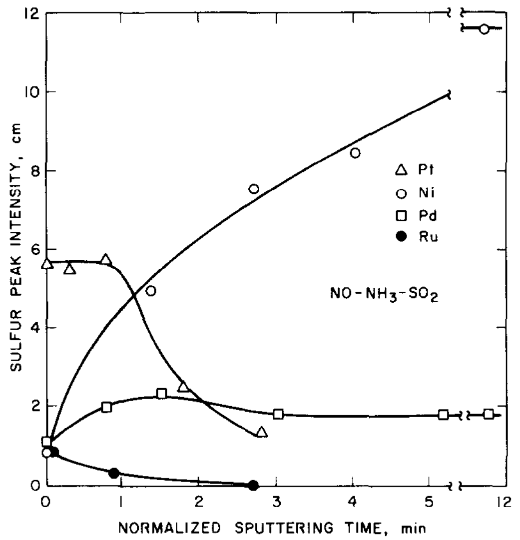

FIG. 9. Sulfur peak intensity as a function of normalized sputtering time for metal foils exposed to NO reduction by NH_3 in the presence of SO_2. Reaction conditions: 400 °C, 1% NO, 1% NH_3, and 250 ppm SO_2 in He, 1 atm total pressure, run duration = 48 hr, Ru data taken at 250°C.

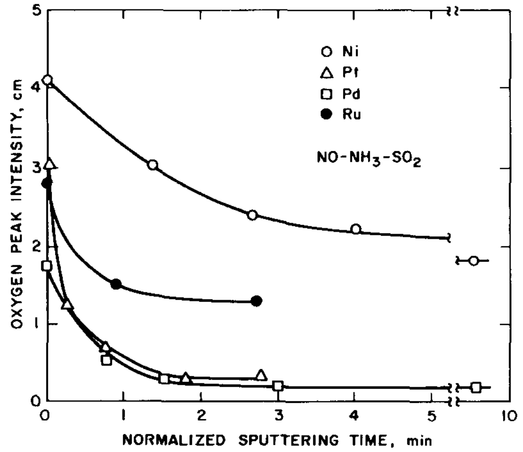

FIG. 8. Oxygen peak intensity as a function of normalized sputtering time for metal foils exposed to NO reduction by NH_3 in the presence of SO_2. Reaction conditions: 400°C, 1% NO, 1% NH_3, and 250 ppm SO_2 in He, 1 atm total pressure, run duration = 48 hr, Ru data taken at 250°C.

For Pt, the data suggest the presence of a highly oxidized surface, perhaps having a composition similar to PtO_2 (oxygen peak intensity = 3.1 cm (Fig. 8), O/Pt = 1.4). Sulfide is also present (sulfur peak intensity = 5.8 cm (Fig. 9), S/Pt = 2.5). A sample of PtS_2 pressed into indium foil was analyzed by AES and gave S/Pt = 2.1 on the surface; this was reduced to about 2.0 with sputtering. It is inferred that the difference in S/Pt peak ratio between PtS_2 and the Pt foil exposed to NO-NH_3-SO_2 is due to further reduced Pt peak intensity for Pt foil because of oxygen incorporation. The oxygen peak intensity decreased rapidly upon sputtering but was still significant (O/Pt = 0.06) after 2 min. The sulfur signal decreased more slowly and was still fairly strong (S/Pt = 0.25) after 2.75 min of sputtering. The oxygen on the surface may have been due to adsorbed SO_X species, to adsorbed oxygen, or to reaction-incorporated oxygen. The absence of any sulfur peak shape changes from surface to subsurface regions suggests that the oxygen signal is due to chemisorbed oxygen. Sulfide peak shapes only were present.

Sulfur (S/Pd = 0.23), as well as oxygen (O/Pd = 0.37), was present on the surface of Pd. The sulfur peak intensities increased and stabilized with sputtering, whereas the oxygen signal intensity rapidly decreased to zero with sputtering (Figs. 8 and 9). Sulfur but not oxygen had been incorporated into Pd; the oxygen is inferred to have been picked up during transfer but could have been adsorbed SO_X species.

Nickel showed different behavior (Fig. 8). The surface was substantially covered with oxygen (nickel oxide) which probably formed during transfer from the reactor to the Auger spectrometer. This can be explained by the relative ease of oxidation of Ni. Other work has shown that nickel surfaces covered with sulfur are subject to easy oxidation in oxygen leading to nickel oxide formation over the metal sulfide but that there is very little sulfur removal (*21, 23*). The sulfur peak intensity grew, as the oxygen peak intensity decreased, and ultimately reached a S (151 eV) to Ni (61 eV) peak ratio of 2.7. Colby (*21, 23*) has shown that a S/Ni peak ratio equal to 1.0 represents one monolayer of sulfur on Ni and that the value of bulk NiS_2 is S/Ni = 4.0. Since ΔH_f^0 for NiO is -58.4 kcal/mole, as compared with the value for nickel sulfide which is about -11 kcal/mole (from H_2S), nickel oxide should be formed more readily than sulfide if there is sufficient oxygen activity. The shape of the sulfur peak after 2 and 10 min of sputtering is shown in Fig. 10. There was no change in S peak shape with depth, and the shape is the same as that observed for Pt.

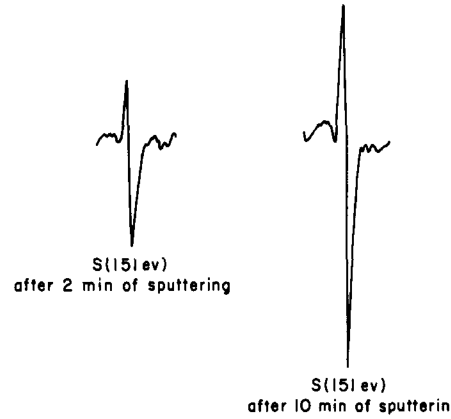

FIG. 10. AES spectra of sulfur on SO_2-deactivated nickel foil after 2 and 10 min of sputtering at standard spectrometer conditions. Nickel foil deactivated for 100 hr at 400°C in 1% NO, 1% NH_3, and 250 ppm SO_2 in He, 1 atm total pressure.

Obviously, for Pt, Pd, and Ni the microenvironment at the surface is sufficiently reducing that metal sulfide and not oxide formed. This is in accord with our observation that in the $NO–NH_3–SO_2–Pt$ system some of the SO_2 was reduced to elemental sulfur, but no detectable H_2S was produced (*24*). For Ni and Pd, with SO_2 alone in He, only oxide is formed; no sulfide is formed (*19*).

In contrast to Pt, Pd, and Ni, Ru foils (250°C reaction temperature) had very little sulfur (S/Ru = 0.14) on the surface, and the sulfur peak intensity decreased to almost zero in 1.0 min normalized sputtering time (Fig. 9). There was considerable oxygen present on the Ru surface (O/Ru = 0.46, Fig. 8) suggesting formation on a surface oxide, and the oxygen signal was sputtered to about one-half its surface value in 1.0 min (Fig. 8). However, there was no further reduction in the oxygen signal with 3 min sputtering, and the intensity of the oxygen signal was three times that in either the "blank" run (Fig. 5) or for the $NO–NH_3$ system (Fig. 7).

Clearly the tolerance of Ru/Al_2O_3 to SO_2 poisoning is due to the lack of sulfide formation and the incorporation of oxygen into the bulk with Ru, in contrast to Pt, Pd, or Ni. This also correlates with our observation that in NO reduction by H_2 in the presence of 50 ppm SO_2 Pt/Al_2O_3 reduced most of the NO to NH_3, whereas Ru/Al_2O_3 reduced very little of the NO converted to NH_3 (*24*). Similarly H_2S was formed over Pt/Al_2O_3 but not over Ru/Al_2O_3. The microenvironment at the surface of the Ru is much less strongly reducing than that of the other metals, and this difference explains the different sulfur poisoning behavior and differences observed in the AES analyses of the Ru foils after reaction. The reducing surface microenvironment is illustrated by the chemical state of the sulfur on the foils. None of the sulfur peaks found in this work were characteristic of sulfate. All surfur peaks, even when a relatively intense oxygen peak was present, were characteristic of metal sulfide.

Further discussion of the above results appears in Tsai *et al.* (*28*) in which the effect of O_2 on SO_2 deactivation in selective reduction of NO by NH_3 is discussed, and the entire set of results is discussed together.

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REFERENCES

1. Sittig, M., "Air Pollution Control Processes and Equipment," p. 5. Noyes Development Corporation, 1968.
2. Shelef, M., and Kummer, J. T., "The Behavior of NO in Heteregeneous Catalytic Reactions." 62nd Annual AIChE Meeting, Paper 13f, Washington, D.C., November 16–20, 1969.
3. Katzer, J. R., *in* "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.), pp. 133–170. Plenum, New York, 1975.
4. Otto, K., Shelef, M., and Kummer, J. T., *J. Phys. Chem.* **75** (7), 875 (1971).
5. Otto, K., and Shelef, M., *J. Phys. Chem.* **76** (1), 37 (1972).
6. Shelef, M., and Gandhi, H. S., *Ind. Eng. Chem. Prod. Res. Develop.* **11** (1), 2 (1972).
7. Anderson, H. C., Green, W. J., and Steele, D. R., *Ind. Eng. Chem.* **53**, 199 (1961).
8. Nonnenmacher, H., and Kartte, K., U. S. Patent No. 3,279,384, October 18, 1966.
9. Bartok, W., Crawford, A. R., Cunningham, A. R., Hall, H. J., Manny, E. H., and Skopp, A., "System Study of Nitrogen Oxide Control Methods for Stationary Sources." Final Report—Volume II. Prepared under Contract Ph-22-68-55 for National Air Pollution Control Administration by Esso Research and Engineering Co., November 20, 1969.
10. Jones, J. H., Kummer, J. T., Otto, K., Shelef, M., and Weaver, E. E., *Environ. Sci. Technol.* **5**, 790 (1971).
11. Pusateri, R. J., Katzer, J. R., and Manogue. W. H., *AIChE J.* **20**, 219 (1974).
12. Meguerian, G. H., Rakowsky, F. W., Hirschberg, E. G., Lang, C. R., and Schock, D. N., "NO_x Reduction Catalysts for Vehicle Emission Control." SAE Paper 720480, May 1972.
13. Campau, R. M., Stefan, A., and Hancock, E. E., "Ford Durability Experience on Low Emission Concept Vehicles." SAE Paper 720488, May 1972.
14. Gagliardi, J. C., Smith, C. S., and Weaver, E. E., "Effect of Fuel and Oil Additives on Catalytic Converters." Paper 63-72, 37th Midyear API Meeting, New York, May 8–11, 1972.
15. Jackson, H. R., McArthur, D. D., and Simpson, H. D., "Catalytic NO_x Reduction Studies." SAE Paper 730568, May 1973.
16. Saleh, J. M., *Trans. Faraday Soc.* **66**, 242 (1970).
17. Saleh, J. M., *Trans. Faraday Soc.* **67**, 1830 (1971).
18. Saleh, J. M., *Trans. Faraday Soc.* **64**, 796 (1968).
19. Gould, R. M., and Huss, A., Jr., B.Ch.E. thesis, University of Delaware, Newark, 1974.
20. Otto, K., Shelef, M., and Kummer, J. T., *J. Phys. Chem.* **74**, 2690 (1970).
21. Colby, S. A., and Katzer, J. R., submitted.
22. Wehner, G. K., *in* "Methods of Surface Analysis" (A. W. Czanderna, Ed.). Elsevier, New York, 1975.
23. Colby, S. A., M.Ch.E. thesis, University of Delaware, Newark, 1977.
24. Foley, J. M., Katzer, J. R., and Manogue, W. H., *Ind. Eng. Chem. Prod. Res. Develop.* **18**, 170 (1979).
25. Markvart, M., and Pour, V. L., *J. Catal.* **7**, 279 (1967).
26. Williams, F. L., and Baron, K., *J. Catal.* **40**, 108 (1975).
27. Farrell, H. H., *Surface Sci.* **34**, 465 (1973).
28. Tsai, J., Agrawal, P. K., Sullivan, D. R., Katzer, J. R., and Manogue, W. H., *J. Catal.* **61**, 204 (1980).